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Concentration of Taylor cones in needleless electrospinning

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ABSTRACT

In this study, I have investigated the effect of Sodium Chloride (NaCl) salt on the spinnability of Polyethylene oxide (PEO) nanofibers and electrical current which is carried on jets via roller (needleless) electrospinning method. At first, solution properties were determined and then the results were analyzed. According to results, NaCl salt concentration has an important effect on conductivity, viscosity, spinning performance, fiber diameter and morphology. Conductivity and diameter of fibers increase with salt concentration. Polyethylene oxide with 0,3wt% NaCl gives the best spinning performance (throughput). During spinning process, process was recorded by camera and electrical current has been measured, afterwards, current, which was carried through per a jet was calculated. Eventually fabric throughput per current carried by Taylor cone was extrapolated.

Keywords:

Electrospinning

Needleless electrospinning

Taylor cone

Throughput

Current

Throughput per Taylor cone

Concentration of Taylor cone

TABLE OF CONTENT

List of abbreviations and symbols:

PEO- Poly (ethylene oxide)

NaCl- Sodium chloride

NFA- non-fibrous area [%]

Wt%- Weight percent

Pas- Pascal second

SI- The International System of Units

SEM- Scanning Electron Microscope

Rpm- Revolution per minute

σ- Standard deviation

π- Pi number

N- Number of measured nanofibers

x_i- Fiber diameter [nm]

μ- Mean of fiber diameters [nm]

P- Polymer throughput [g/min/m]

G- Weight of nanofibers membrane per area [g/m^2]

w_F- The width of nanofibers membrane [m]

l_{R-} The length of spinning roller [m]

P_c- Thoughput per cone [(g/min/m)/N]

N_c- Number of cones

μA- Microamper

I- Current [μA]

Q- Feed rate [ml/hour]

κ- Solution conductivity [mS/cm]

D- Density of Taylor cones [cm^{-2}]

n- Number of imaginary square surrounding one Taylor cone

x- Distance between Taylor cones [cm]

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1. INTRODUCTION

1.1. Electrospinning of nanofibers:

The electrospinning of nanofibers is a novel process for producing ultra superfine fibers by forcing a solution through a spinneret with an electric field. An emerging technology of manufacturing of thin natural fibers is based on the principle of electrospinning process. In conventional fiber spinning methods, the mechanical force is applied to the end of a jet. Whereas in the electrospinnig process the electric force acts on element of charged fluid [Ramakrishna et al. (2005)].

A high voltage is applied to a polymer fluid where the charges are induced within the solution. When charges in the solution reach a critical amount, the fluid jet will erupt from the polymer solution in the formation of a Taylor cone. The electro spinning jet will travel towards the region of lower electrical potential, which is mostly a grounded collector.

Electrospinning has emerged as a specialized processing technique for the formation of sub-micron fibers, typically between 100 nm and 1 μ m in diameter (the academic community has somewhat agreed to the <100nm criterion as the benchmark for the nanotechnology classification, the commercial sector has allowed wider flexibility, such as 300nm or even up to 500nm, which some academics would classify as sub-micro technology), with high specific surface areas. Due to their high specific surface area, high porosity, and small pore size, the unique fibers have been suggested for wide range of applications. The morphology of the electrospun fibers such from fibers with pores on its surface to beaded fibers, are changed by many parameters [Ramakrishna et al. (2005)].

Nanofibers are in atomic scale which is about 10 times of Hydrogen atom. One atom is 0,3nm, nanofibers are 50-1000nm, synthetic fibers are 2000-5000 nm, one blood cell from human body is 5000nm, 1,5 denier conventional fiber 12500 nm and a human hair is between 20000-30000nm [Callioglu, F. C. (2011)]

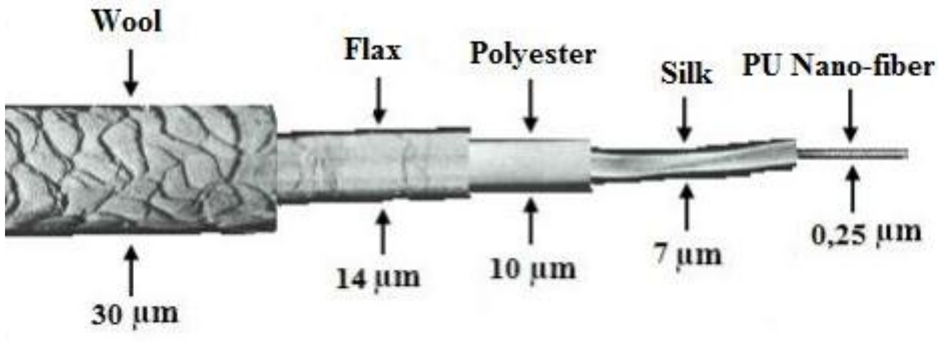


Fig. 1- Comparison of the different fiber diameters

Source:[Callioglu, F. C. (2011)]

It is typical for the electrospinning of a polymer solution, as the voltage increases above the critical value, initially a straight jet is formed from the Taylor cone. The electrically charged polymer jet travels towards the grounded collector in a straight line for few centimeters and at the end this segment, a conical shape, a complicated path taken by jet, can be observed. Electrospinning is a quite quick process. Because there is extremely fast whipping of the jet, after a completed 1ms, only the conical shape of spraying of solution from the jet have been observed [Tao, J.(2003)]

1.2. Historical development of electrospinning:

The first documented accounts of electrostatic spinning of a polymer solution into nanofibers were described in 1902 by J. F. Cooley and by W. J. Morton. Theoretically, between 1964 and 1969, Sir Geoffrey Ingram Taylor contributed to electrospinning by mathematically modeling the shape of the cone formed by the fluid droplet under the effect of an electric field; this characteristic droplet shape is now known as the Taylor cone. Then others followed (see Table 1). [Dao, A. T. (2011)]

Nowadays, Nano spider is the unique commercial equipment to produce nanofibers web via needless electrospinning technology. This equipment is first patented by Prof Jirsak from Technical university of Liberec, and then it is developed by Czech company Elmarco, makes possible to use in industrial production of non-woven textiles with high production rate.

Table 1 - A brief list of chronological development of electrospinning patents

YEAR	INVENTOR	PATENT NO
1902-1903	Cooley, J. F.	U.S. pat. #s 692,631; 745,276
1902	Morton, W. J.	U.S. pat. # 705,691
1934-1944	Formhals, A.	U.S. pat. #s 1,975,504; 2,077,373; 2,109,333; 2,116,942; 2,123,992; 2,158,415; 2,158,416; 2,160,962; 2,187,306; 2,323,025; 2,349,950
1929	Hagiwara, K.	U.S. pat. # 1,699,615
1936	Norton, C. L.	U.S. pat. # 2,048,651
1939	Gladding, E. K.	U.S. pat. # 2,168,027
1943	Manning, F. W.	U.S. pat. # 2,336,745
1966	Simons, H. L.	U.S. pat. # 3,280,229
1976-1978	Simm, W., et al.	U.S. pat. #s 3,944,258; 4,069,026
1977-1978	Martin, G.E., et al.	U.S. pat. #s 4,043,331; 4,044,404; 4,127,706
1980	Fine, J., et al.	U.S. pat. # 4,223,101
1980-1981	Guignard, C.	U.S. pat. #s 4,230,650; 4,287,139
1982-1987	Bornat, A.	U.S. pat. #s 4,323,525; 4,689,186
1985	How, T. V.	U.S. pat. # 4,552,707
1989	Martin, G. E.,	U.S. pat. # 4,878,908
1991	Berry, J. P.	U.S. pat. # 5,024,789
2000	Scardino, F. L. And Balonis, R. J.	U.S. pat. # 6,106,91
2004	Chu, B., et al.	U.S. pat. # 6,713,011

Source: [Andrady, A. L. (2008)]

1.3. Application fields of nanofibers:

Electrospinning is relatively cheap process and unequivocal method, comparing with traditional methods. Also it has gained lot of considerations during the last few years and it is still rising.

Nanofibers are getting to be more common day by day, always some new fields are opening for the usage of nanofibers. Survey for uses of nanofibers can be classified as following; Tissue engineering scaffolding (Porous membrane for skin, Tubular shapes for blood vessels and nerve regenerations, Three dimensions scaffold for bone and cartilage regeneration), Applications in life science (Drug delivery carrier, Haemostatic devices, Wound dressing), Cosmetic skin mask (Skin cleaning, Skin healing, Skin therapy with medicine), Military protecting clothing (Minimal impedance to air, Efficiency in trapping aerosol particles, Anti-biochemical gases), Nano sensors (Thermal sensors, Piezoelectric sensors, Biochemical sensors, Fluorescence optical chemical sensors), Filter media (Liquid filtration, Gas filtration, Molecule filtration), Other industrial applications (Micro/nano electronic devices, Electromagnetic interference shielding, Photovoltaic devices, LCD devices, Ultra-lightweight spacecraft materials, Higher efficient and functional catalysts). [Dao, A. T. (2011)]

1.4. Aim of the work:

Needleless electro spinning is a quite new technique. As it is expensive and time consuming process so the objective of this work is to find some type of relationship between process mechanism, process parameters and polymer throughput so that productivity of needleless electrospinning can be increased by changing Polymer solution properties. The central point of experimental work will be to test poly (ethylene oxide) with different polymer concentrations and changing addition of NaCl salt, whereas the ambient parameters (temperature and humidity), molecular weight, voltage supply and distance between electrodes were kept constant. Process will be recorded by camera and pictures of process will be analyzed to find out spinability, throughput, number of Taylor cones and density of Taylor cones. The result will be examined on SEM to find electrospinning particularly in terms of, fiber quality, fiber diameter, non-fibrous area and fiber diameter distribution.

2. THEORETICAL PART

2.1. Electrospinning process:

Electrospinning process has been developed for many years; therefore improvements always have been sought in the apparatus, in the process and in the polymers. Most commonly used devices for electrospinning can be divided to 2 main groups: needle electrospinning and needleless electrospinning. And in our university, needleless electrospinning devices are classified into 2 sub-groups: rod electrospinning and rotating cylinder (roller) electrospinning.

Needle electrospinning is used popularly in laboratories by researchers. Polymer solutions are easily spun and controlled in needle electrospinning and wanted properties are reached. But it has its own disadvantages, there is only one jet per needle and the spinning area is very small (0.5 -1 mm^2). [Dao, A. T. (2011)]

In needleless electrospinning, in case of rod system, there are only few fibers occurring from the tip of rod and this system is generally used for laboratory purposes such as determine the spinnability of the polymer solution. However, during electrospinning with the roller system, there are several jets, usually 3000-45000 jets in square meter of the surface of roller which is electrode of electrospinning. [Dao, A. T. (2011)]

This process can be divided into three stages. During first stage, polymer solution is fed by pump in the needle electrospinning process or by roller from container in the needleless electrospinning. Jet formation occurs, when the solution is charged by high electric potential. The jets (or jet in needle electrospinning) are discharged from the roller's surface or from the needle tip. This cause, the jets will regularly accelerate and thin out along an axis aligned with the general direction of the electric field. In this stage, the stability and the results of the stage control all its following stages and at the end, the desired properties of the finished fibers. In the second stage, the changes of the electric lines, caused by time and space variation of the density of electrical charges, induces jets to turn transversely to the field direction. This produces a cloud that expands toward the collector by action of same polarity charges. Meanwhile, since vaporization of the solvent has started in first stage, it develops during this stage, the jet solidifies and the resulting fibrous cloud drifts in the applied electric field to the collector. An unsteady bulk fiber mesh structure might be done by that the jet may endure a sequence of splitting at second stage. Third stage consists of two processes: random deposition of fibers into a layer on collector and second, discharge between collector and the fiber layer that closes the electric circuit. [Dao, A. T. (2011)]

2.2. Needleless electrospinning:

2.2.1. Rod electrospinning:

In rod spinning (Fig.2.B), a metal rod is used as a spinning electrode across the grounded collector in perpendicular direction. Rod diameter has an massive effect on number of Taylor cones, if the diameter of the metal rode, there for diameter of polymer solution droplet, is greater that 8mm, 1 till 6 Taylor cones , if rod diameter is 3mm or less, there can be only one Taylor cone [Pokorny et al. (2010)].

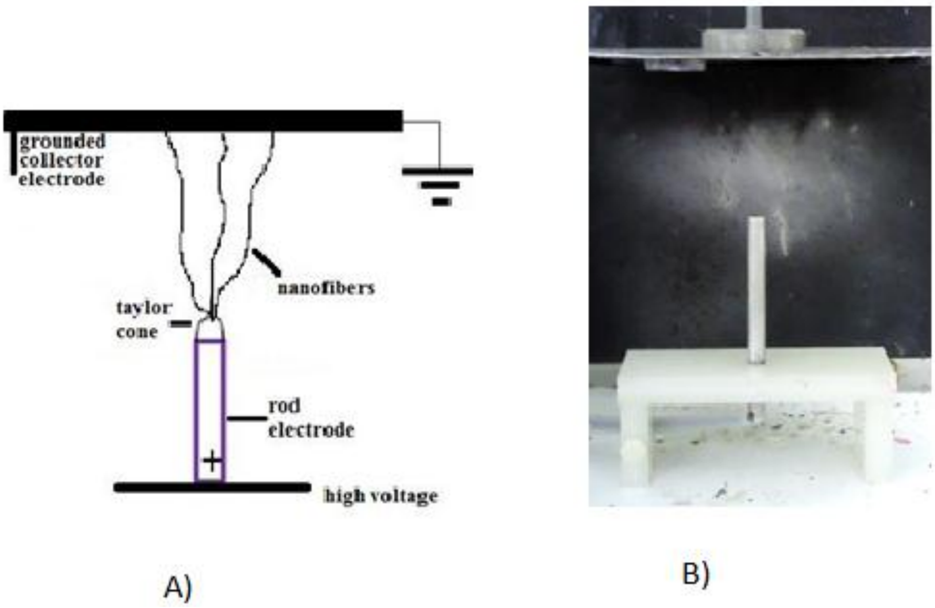


Fig. 2 - Rod electrospinning apparatus and Electrospinning device consisting of a rod and its collector.

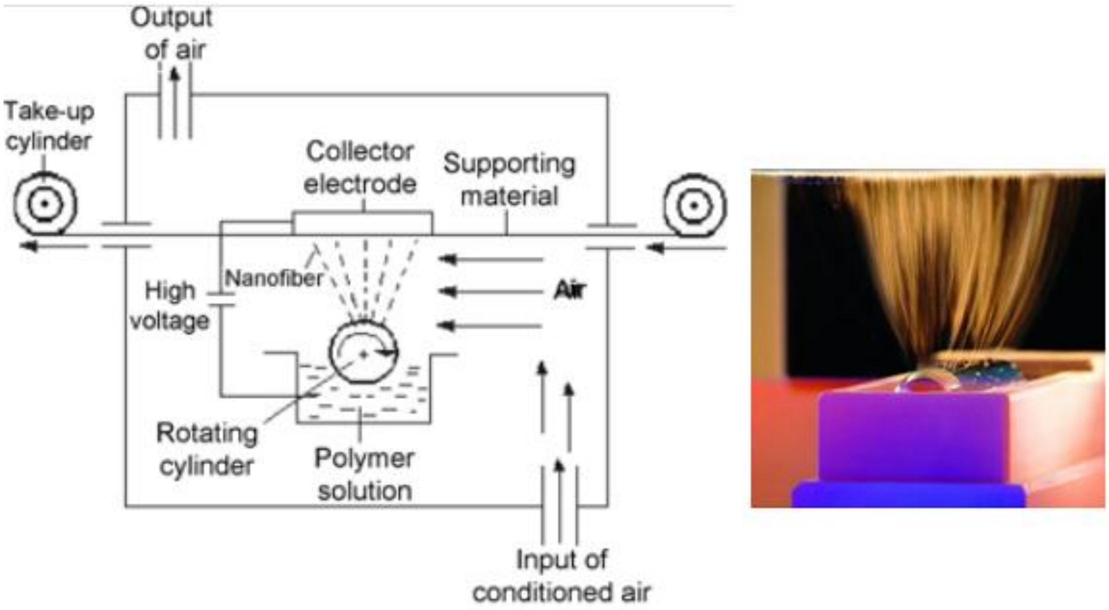
Source: A) [Callioglu, F. C. (2011)] B) picture-taken by me

For production of nanofibers, one drop of polymer solution is dropped on the tip of rod electrode as in the sketch Fig.2.A. With this method, as other (needle, roller etc) methods, high voltage is applied to a drop of polymer solution which is stated o the tip of rod electrode. Created nanofibers are collected on to collector electrode plate placed in a constant distance. [Lukas et al,2009]. In this method, different than other methods, only small amount of polymer solution can be spun, that is why this method is used to figure out polymer solution's spinnability and analyze Taylor cone instead of collecting fibers.

2.2.2. Roller electrospinning:

In needleless electrospinning, roller, which is partially immersed into polymer solution, rotates slowly and during electrospinning process, polymer solution is taken to the surface of the roller because of its rotation. Many of Taylor cones are simultaneously created on the roller surface and produce nanofibers by using suitable high voltage. The nanofibers are then transported towards the collector in against to gravity [A.T. Dao & O. Jirsak (2009)]

The Fig. 3 is the sketch and a picture of the needleless (roller) electrospinning apparatus.



A) **B)**

Fig. 3 - Schematic diagram of nanospider method (a), the rotating cylinder (b)

Source: A)[Dao,A.T. (2011)], B) [Anon. (2004)]

For my thesis, I have worked with roller electrospinning, therefore after this point I will focus on roller spinning process.

2.3. Parameters of Roller electrospinning:

There are some various parameters which influent the electrospinning process and products. Even thought there is very wide range of variation of parameters, for simple explanation, they can be divided in to two main groups as dependent and independent parameters.

Dependent parameters of the electrospinning process are fibers diameter (nm), number of beads on the nanofibers membrane, size of beads (nm^2) and length of jet (m). These parameters are affected by independent parameters. Independent parameters are listed as following:

-Material parameters: own properties of the polymer or copolymer, including type of polymer, polymer blends and additives, solution parameters which are zero shear viscosity (Pas), concentration of polymer solution(%), conductivity (mS/cm), surface tension (mN/m), molecular weight, solvents and mixture of solvents and/or additives etceteras.

-Process parameters: These parameters explain influence of environment and process itself; that include applied electrical voltage (kV), current (A), velocity of roller (rpm), distance between electrodes (mm), relative humidity (%), temperature (^oC), speed of collector electrode (cm/min). These parameters affect the spinning process and the properties of the product [Dao, A. T. (2011)].

2.3.1. Independent parameters:

2.3.1.1. Material parameters:

Zero-shear viscosity:

In electrospinning process, solution viscosity is a parameter which states if the process will occur or not, and also it has important effect on fibers diameter and morphology of the products [Dao, A. T. (2011)]. A higher viscosity results in a large fiber diameter or it is difficult to get jet from polymer solution; and in opposite cases, when viscosity of polymer solution is too low it becomes electro spraying instead of electrospinning and polymer particles can be formed instead of nano fibers or nano fibers with beads are developed [Ramakrishna et al. (2005) ; Andrady, A. L. (2008)].

“The viscosity of water at 20^{o} C is about 1.00cP whereas that of olive oil is about 10,000 cP at the same temperature.” is said by Andrady, A. L. (2008). As the Fong and his co-workers have reached the result of nanofiber form from Polyethylene oxide (PEO) solution which has viscosity range between 1 and 20 poise that is suitable for electrospinning.

Concentration of solution:

For best spinning process, the optimum polymer solution’s concentration must be found. Because if the concentration is too high, viscosity resistance gets higher too accordingly fiber diameters increase [Dao, A. T. (2011)]. In the same time high concentration means; viscosity of the polymer solution is enough strong to resist instant stability changes, thus fibers may form uniformly. If the concentration of the solution becomes so high, that leads to difficulty in jet formation which makes the electrospinning impossible [A. K. Haghi and M. Akbari (2007)].

Conductivity:

The electro spinning process requires the transfer of electric charge from the roller to the spinning droplet at the end of the tip. Solution without conductivity cannot be electrospun therefore it is necessary to have at least minimal electrical conductivity in the solution. Common solvents which are used for electrospinning have conductivities which are lower than the conductivity of the distilled water[1].While increasing polymer concentration in solution, however, it is possible solution’s conductivity would decrease [Jun et al. (2003)]. When there is use of ionic polymers (as with polyelecrolytes), the conductivity of the solution will be high and depend on the concentration [McKee et al. (2006)].

Conductivity is the contrary of the resistance (R) which is described with Ohm law, and generally symbolized with G. According to this, as the solution’s resistance decreases, conductivity of the solution increases. Since the unit of resistance is ohm (Ω), the unit of conductivity is ohm^{-1} and this unit is named of Siemens (S) and $S=\Omega^{-1}$ [Sarikaya, Y. (2005)].

[1] The SI unit for conductivity is siemens per meter, where 1 siemen = 1 ampere/volt $=(\Omega)^{-1}$

Surface tension:

Surface tension is the force opposing coulomb repulsion [Andrady, A. L. (2008)]. in other words the surface tension of a fluid is force acting at right angles to any line of the unit length on the liquid surface. In electrospinning, the charge on the polymer solution must be enough high however can break the surface tension of the solution and allow the solution jet be spun. When the solution jet accelerates from the roller to the collector, mean time, polymer solutions surface tension might be reason of splintering into beads/droplets [Schummer, P. and Tebel, K. H. (1983); Christianti Y. and Walker M. (2001)]. In case of reducing surface tension of solution, created nano fibers can be realized without beads. Different solvents may have different surface tensions [Hohman et al. (2001)].

Molecular weight:

Polymer, as it is apparent from the name, is molecule chain which is made up of multiple repeating molecules. There for the molecular weight of the polymer is the sum of the individual monomers' molecular weight. The molecular weight of the polymer influences its viscosity in such a way that as molecular weight goes higher, viscosity goes higher [Ramakrishna et al. (2005)]. Where high molecular weight solutions give large diameters, low molecular weight solutions try to form beads instead of fibers.

Volatility (evaporation) of solution:

In the electrospinning process, when the electrospinning jet accelerates towards the collector, the solvent will evaporate from the solution. As the jet reaches the collector, most of the solvents have evaporated and individual fibers are formed. Nevertheless, in case of that evaporation of the solvent is very low that solvent cannot evaporate adequately when the electrospinning jet reaches the collector, fibers may not be formed at all and a thin film of polymer solution is deposited on the collector [Ramakrishna et al. (2005)].

Solvent volatility is a key consideration in controlling fiber diameter. With a suitable selection of solvents and process parameters, extra fine nanofibers[2] can be spun [Andrady, A. L. (2008)].

[2] Extra fine Nanofibers, with diameters in the 1–2 nm range have been electrospun from solutions of nylon (Huang et al. 2006). Burger et al. (2006) estimated that a nanofiber 100 nm in

2.3.1.2. Process parameters:

Applied voltage:

As it is seen from the name of this process – electrospinning - one of the most important parameters of the electrospinning process is electric, that is applied voltage. It is the all energy for spinning system. Applied voltage is obligation for this process, without applied voltage, the electrospinning process cannot occur. The high voltage will induce the necessary charges on the solution together with external electric field, when the electrostatic force in the polymer solution overcomes the surface tension of the solution, electro spinning process performs. Generally, high negative and high positive voltage which is more than 6kV is able to cause to deform into the shape of Taylor Cone at the tip of the needle during jet initiation. [Taylor, I. G. (1964)]. When the applied voltage is higher, bigger amount of charges will cause the jet to be quicker and more solution will be drawn from the system. This may cause, Taylor cones will be smaller and less stable [Zhong et al. (2002)].

In electro spinning, the fluid jet travels toward the distance between highly charged electrode and grounded collector plate. Surface charge is responsible for the acceleration of the initial jet heads the collector. During the process as there is mass transfer, there is a corresponding charge transfer crossing the gap. The current flow due to this transfer can be measured and it is generally found to increase smoothly with the applied voltage [Samatham, R. and Kim K. J. (2006)].

Current:

Electric current is a flow of electrical charge through a material. [Lakatos et al. (1998)]. Measurement of current is described as the voltage drop across the resistor placed with series connection between electrode and ground [Shin et al. (2001) and Deitzel et al. (2001)]. Some authors [Kim at al. (2005)] places microammeter at the same position instead of resistor. In my work I have measured current to reach the relation between current and throughput.

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diameter stretched from the Earth to the Moon (a distance of 380,000 km) would have a mass of only ~3 g.

Current is explained by Ohm Law:

$$"I = U/R"$$

Equation 1 – Ohm Law

I is the current, measured in microampers, U is the potential difference measured in volts and R is the resistance measured in ohm.

Velocity of roller:

Mission of the roller (in other words rotating cylinder) is supplying the polymer solution during electrospinning process. The velocity of the roller will arrange amount of solution taken from the tank and supplied to spinning area. Thickness of the solution layer on the cylinder is related to its velocity along other features like viscosity of the polymer solution, temperature…etc, but normally, in same conditions, the one which has higher velocity of the rotating cylinder also has thicker layer of polymer solution around the roller and the greater amount of solution is supplied for spinning. That is why this parameter affects the number of jets and life time of jet [Dao, A. T. (2011)]. Through number of jets, I aimed to reach current per one Taylor cone.

Distance between electrodes:

The distance between the roller and collector has a role in controlling the fiber diameters and the morphology. Minimum distance is required to give fibers enough time to dry before reaching the collector, with either too close or too far distances, beads are observed. There should be an optimum distance between the tip and the collector which will allow the evaporation of solvent from the nanofibers [Dao, A. T. (2011)]. In order to have a well created nanofibers membrane's throughput, distance between electrodes is an important parameter. Eventually current is compared with fabric throughput for this work.

Types of Collector electrode:

One important aspect of the electrospinning process is the type of collector used. In this process, a collector serves as a conductive substrate where the nanofibers are collected. Aluminum foil, conductive paper, conductive cloth, wire mesh, pin, parallel or grid bar, rotating rod, rotating wheel, liquid non solvent such as methanol coagulation bath and others are also common types of collectors nowadays. However, the collector for roller electrospinning is quite simple. There is a rectangular metal plate, above the roller, which is grounded and a running collector fabric which is moving along the collector and collecting the nanofibers on its surface [Dao, A. T. (2011)]. There are also other types of collector electrodes for roller spinning are developed and tested, but for this work the one is described is used. Due to its easy afterward process for calculation of fabric throughput.

Velocity of running collector fabric:

In needleless technique of electrospinning process, a collector fabric is running above the spinning roller, under the collector electrode (between collector and roller) in order to collect nanofibers. The velocity of this fabric (meters per minute) influences the density of the nanofibers layer and so the areal weight of the produced nanofibers fabric. This also affects to quality of the nanofibers membrane and non-fibrous area [Dao, A. T. (2011)]. Weight of nano fibers web is one of the parameters which is used for calculation of fabric throughput.

Ambient parameters (temperature and humidity):

The temperature of the solution has an effect on both increasing its evaporation rate and reducing the viscosity of the polymer solution. [Demir et. al. (2002)]. In high temperature, viscosity of the solution is lower and solubility of the solution is greater and that allows more even stretching of the solution therefore produced fibers have more uniform diameter. With a lower viscosity, the Columbic forces are able to expert a greater stretching force on the solution thus fibers have smaller diameter [Mit-uppatham et. al. (2004)].

If there is very low humidity, a volatile solvent may dry out quickly as the evaporation of solvent is faster.

2.3.2. Dependent parameters:

Parameters about produced nanofibers membrane are so called dependent parameters. These parameters change the total surface area of nanofibers, diameter of fibers and bead formation on fibers therefore on nanofibers fabric. Dependent parameters are concern for fabric morphology studies. This is not the subject of this study.

Density of cones:

In roller electrospinning, numerous Taylor cones appear on spinning area during the electrospinning process. The density of cones can be determined from the camera records or taken pictures as a number of Taylor cones (N) per area (A- m^{-2} or cm^{-2}). Density of jets, synonymously density of Taylor cones, is an important parameter in the needleless spinning process. It is related to solution properties, electrical field strength, the spinning performance and the average life time of jets.

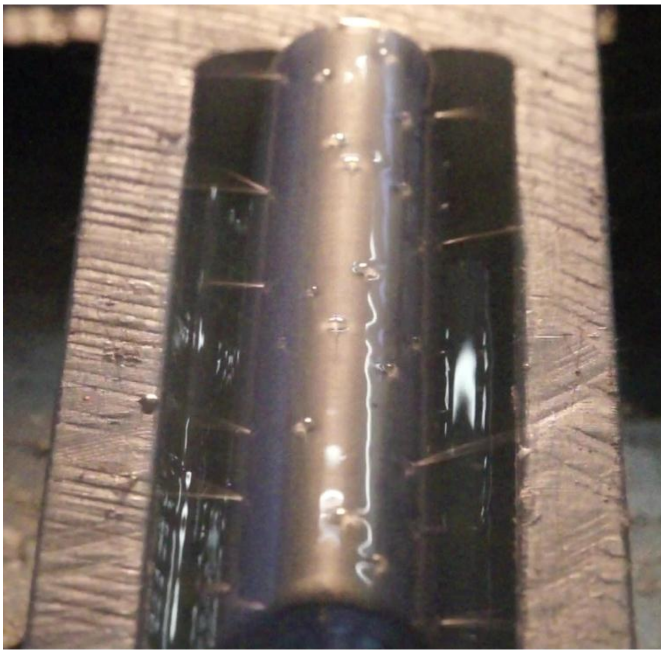

Fig. 4 - Determination of number and density of Taylor cones during the electrospinning process
Source: picture- taken by me

The spinning process will be recorded by camera to determine the density of cones. Plenty of pictures were taken from camera record due to calculate average value of number of cones. The number of Taylor cones (N_c) was counted from these pictures as shown in Fig. 4. The density of cones (D) will be calculated as the ratio number of cones (N_c) to the spinning area (A). Even though spinning area is described as a one third of surrounding area of roller, from the pictures I have recorded, the real area of spinning is elsewise. Therefore area of spinning (A) will be particularly measured during the work for each solution. Formulas are following:

$$D = \frac{N_c}{A}, \quad (1/m^2)$$

Equation 2 – Equation of density of Taylor cones

Life time of jet:

The period of time from the point when the jet appears to the point when the jet disappears, describe the life time of the jet [Dao, A. T. (2009)]. During needleless electrospinning process, there isn't only one jet, there are several jets on the roller and life time of the jets is different from one to other. Life time of the jet depends on polymer solution, on position of the jet on the roller electrode, on number of jets, on environment…etc. Calculating the average life time of different jets from different positions in different time during spinning process will give the life time of the jet in spinning process. [Dao, A. T. (2009), Lee, E., J. (2006)]

The life of Taylor cones is affected by the stability of the jet. The jet must be strong enough to stabilize Taylor cone by mechanical forces as it is pulled towards the collector electrode. As soon as the jet breaks, Taylor cone disappears. However the spinning process doesn't continue. A stable Taylor cone is able to bear a jet for from few seconds to tens of seconds. The jet is stronger by salt [You et. al. (2006)]

Long lasting Taylor cone means continuous process; therefore fabric through put will be higher and respectively fabric throughput per cone will be higher.

Fiber diameter

Diameter of fibers of electrospinning process is an important parameter to evaluate the quality of the nanofibers fabric structure. Membrane with fibers with smaller diameter has more surface area than membrane with fibers have greater diameter in constant area. Fiber diameter is affected by many properties, like viscosity, surface tension, distance between roller and collector. A longer flight time will allow more time for the fibers to stretch and elongates before it is deposited on the collector. Also, at lower voltage, the reduced acceleration of the jet and the weaker electric field may increase the flight time of the electrospinning jet [Zhao et. al. (2004)].

Fiber diameter distribution:

Diameters of fibers aren't exactly same. This difference between fibers diameter, in other words fibers diameters distribution can be shown by the fraction of groups of diameters or in deviation value. The smaller deviation, the greater number of fibers had their diameters close to others [Dao, A. T. (2011)]. Standard deviation can be calculated using the equation 3.

$$\sigma = \sqrt{\frac{1}{N}\sum_{1}^{N}(x_i - \mu)^2}$$

Equation 3 – Equation of standard deviation

$$\mu = \frac{1}{N}\sum_{1}^{N} x_i$$

Equation 4 – Arithmetical mean

Where σ is standard deviation, N is number of measured nanofibers, x_i is diameter of nanofibers and μ is average (arithmetic mean) diameter of nanofibers.

Polymer throughput (P):

Spinning performance or fabric throughput is one of the most important characteristics of needleless electrospinning. Throughput, in other words transmission performance, describes the mass of produced material produced by the specific spinning equipment in time. As opposite of the needle electrospinning, in needleless electrospinning the spinning performance is a dependent variable. Determination of throughput is the mass of nanofibers produced in one minute and recalculated per one meter long roller spinning electrode. In practical applications, spinning performance is calculated from area weight of produced nanofibers layer [Dao, A. T. (2011)]. Formula follows:

$$P = \frac{G * v * w_F}{l_R}, \quad [g/min/m]$$

Equation 5 – Equation of polymer throughput

Where P is polymer throughput or spinning performance (*g/min/m*), G is weight of nanofibers membrane per area (g/m^2), v is velocity of running collected fabric (*m/min*), w_F is the width of nanofibers membrane (*m*), l_R is the length of spinning roller (*m*).

Polymer throughput per cone:

The spinning ability of one jet during the spinning process is called spinning performance per cone (P_c). It can be determined by amount of polymer passing through one Taylor cone in time. Its relation with throughput parameter is strong. This relation is shown in formula below:

$$P_c = \frac{SP * l_R * 60}{N_c}, \quad [g/h]$$

Equation 6 –Equation of throughput per come

Here P_c is polymer throughput or spinning performance (*g/min/m*) per Taylor cone, l_R is the length of spinning cylinder (roller) (*m*) and N_c is number of cones during the electrospinning process. [Dao, A. T. (2011)]

Non- fibrous area (NFA):

The quality of the nanofibers membrane can be estimated from this important property of nanofibers membrane. At the same time NFA value refers to the quality of the electrospinning process. The NFA is the area ratio of non-fibrous area in the membrane to total area of product. This can be expressed as percentage or dimensionless. Calculation can be like following equation 7:

$$NFA = \frac{total\ area\ of\ non-fibrous\ area}{total\ area\ of\ nanofibers\ membrane} * 100, \quad [\%]$$

Equation 7 – Equation of non-fibrous area

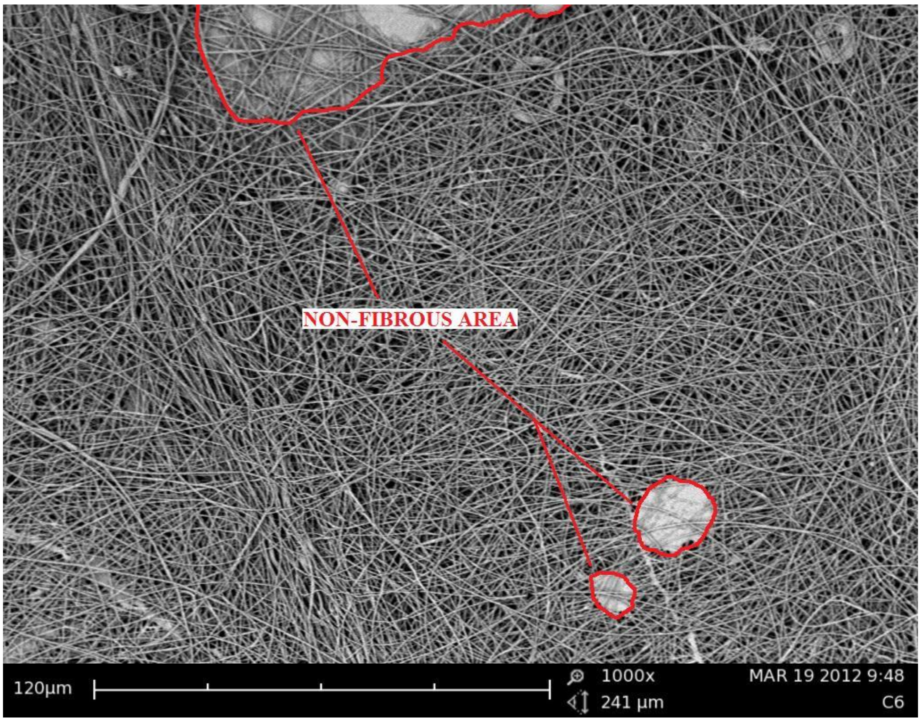

Fig. 5 - Non-fibrous area of the electrospun sample captured with SEM and analyzed with Nis-Elements

Source: Picture- taken by me

From SEM pictures (see Fig. 5) we can measure non-fibrous area on the surface of sample by using Nis-elements software. Then total area of the sample is measured. After all measurements we use formula above to calculate non-fibrous area.

2.3.3. Known relations between independent and dependent parameters:

Independent parameters (process parameters and solution parameters) have effects on dependent parameter. Affects of process parameters: fiber diameter decreases with increasing of applied voltage, bead formation occurs with too small or too great distance, higher ambient temperature results lower fiber diameter, high relative humidity results in circular pores on the fibers. Affects of solution parameters: if viscosity or/and polymer concentration increases fiber diameter increase too, fiber diameter decreases as conductivity increases.

2.4. Summary of theoretical part and objective settings:

Parameters of electrospinning can be classified into two groups: independent parameters and dependent parameters. Following Table 2 summarizes these parameters.

Table 2 - Electrospinning parameters

Independent parameters	**Dependent parameters**
Concentration of polymer solution [%]	Density of Taylor cones [cm^{-2}]
Molecular weight of polymer [g/mol]	Life time of jets [s]
Viscosity of polymer solution [Pas]	Electrical Current [μA]
Conductivity of solution [mS/m]	Throughput [g/min/m]
Surface tension of solution [mN/m]	Throughput per cone [(g/min/m)/N]
Applied voltage [kV]	Non-Fibrous area [%]
Velocity of roller [rpm]	Fiber diameter (nm)
Distance between electrodes (mm)	Fibers diameter distribution
Velocity of running collector fabric (m/min)	
Temperature (^{o}C) and Relative humidity (%)	

Source: The table is created by me

The literature review above shows that the electrospinning technique has been studied for a long time and until now there a great number of researchers dealing with electrospinning because of its potential applications. Factors affecting the electrospinning process and its product have been studied in many works. For instance, affects of solution’s properties (viscosity of solution, concentration of solution conductivity of solution, surface tension of solution, etc.) on product properties and affect of process parameters (applied voltage, distance between electrodes, velocity of roller, temperature, humidity, etc.)

It is the aim of author to define independent and dependent parameters of needleless electrospinning based on his own experiments. Also, the method to measure the parameters will be suggested and/or developed such as current test and high speed usage of camera to identify concentration of Taylor cones. So works in this thesis include:

- Method to measure the parameters will be described in chapter 3.

- The effects of polymer concentration of PEO solutions on some dependent parameters (throughput, throughput per cone, concentration of Taylor cones, etc.)
- The effects of NaCl concentration in solutions, along with conductivity of solution, on some dependent parameters (throughput, throughput per cone, concentration of Taylor cones, etc.)
- Relation between current and throughput of needleless electrospinning will be detected.

3. EXPERIMENTAL PART

3.1. Overview of experiments:

Materials and methods, which are used in the experiments, are described in this part with consideration of needleless electrospinning parameters.

1. Poly (ethylene oxide) with different weight concentrations of solution will be used as materials for the experiment. The aims of these experiments are to explore relationships between concentration of solution and some dependent parameters for example density of cones, polymer throughput and polymer throughput per cone.

2. Effect of solvent property on the needleless electrospinning will be studied. Water-Sodium chloride (NaCl) solution in different ratios will be used as in the solvent of PEO solution. Water is a good solvent of PEO and NaCl increases the conductivity of the solution. Sodium chloride, in different concentrations, will be added to change conductivity of PEO solution. Effect of solution conductivity on some parameters of roller electrospinning will be studied. The effect of the solution's conductivity on some dependent parameters as fabric throughput, throughput per cone, current per cone, density of cones and life time of will be studied in this experiments.

3. Transmitted current by each Taylor cone will be calculated in order to reach optimum production. For this calculation firstly, current flow during the process will be measured then whole current will be divided to throughput and throughput per Taylor cones.

3.2. Material:

Poly (ethylene oxide) (PEO) is a water-soluble synthetic polymer. Other solvents of it; Benzene, alcohols, chloroform, esters, cyclohexanone, N,N- dimethylacetamide, acetonitrile, water (cold), aqueous K_2SO_4 (0.45M above 35^oC), aqueous $MgSO_4$ (0.39M above 45^oC) and nonsolvents are ethers, dioxane (sw), water (hot), aliphatic hydrocarbons. Class of PEO is Polyethers. Poly (ethylene oxide)'s chemical structure:

$$-[CH_2-CH_2-O]_n-$$

Equation 8 – Molecular formula of PEO

Its major applications of PEO are in fields of textile applications, fiber and water retention, cosmetics, antifoaming agents, chemical intermediates, ink and dye solvents, demulsifiers, plasticizers, flocculent, thickening, lubrication, dispersing, it can also be applied to industries like medicine, fertilizer, pulps, ceramics, detergent, cosmetics, heat treatment, water treatment, fire fighting and oil exploration etc. It is non-toxic, non-irritant, and it will not generate residue, sediment and vaporous elements. etc. [Hohman et al. (2001)].

Nowadays, PEO become one of the most popular materials in the electrospinning field. During this work, PEO produced by the Aldrich Company was used. In different concentration of PEO samples, which have 400.000 g/mol molecular weight, were taken into experiments. Different weight concentrations (3%, 4% and 5%) of PEO were used to see the effect of concentration on the Taylor cone and the fabric performance.

3.3. PEO in solution with different NaCl salt concentrations

Salt and water solution has naturally high conductivity. Therefore during this experiment I used Sodium chloride NaCl salt from the company Aldrich, quality p.a as a factor to change the quality of solvent conductivity for PEO polymer solution. Different concentrations of NaCl in PEO solution were used as the solution material for roller electrospinning process. In this experiment I have added NaCl weight concentration rate from 0,1wt% to 2wt% only the solutions of 4% and 5% PEO.

Here below (Table 3) is shown which salt concentrations were used with which polymer concentration solution.

Table 3 - Salt concentrations used with various polymer concentration solution

Polymer (PEO) concentration [w%]	NaCl Salt Concentration [w%]						
	0%	0,1%	0,3%	0,5%	1%	1,5%	2%
3%	✓	-	-	-	-	-	-
4%	✓	✓	✓	✓	✓	✓	✓
5%	✓	✓	✓	✓	✓	✓	✓

Source: My own data, table- created by me

3.4. Measurement Devices:

Before starting the needleless electrospinning process; surface tension, conductivity and zero shear viscosity have been measured. Deeper descriptions of devices are following.

3.4.1. Surface tension:

Surface tension of solutions has been measured by platinum plate method with Krüss brand, Digital Surface Tensiometer K9 (Fig. 6) apparatus. Bottom side of platinum plate gets into contact with measured liquid. Liquid climbs up and starts to drag platinum plate in to polymer solution. Wilhelm force, created by wetting, is measured by pulling the platinum desk out back to surface of liquid. Platinum plate can be kept in zero distance with polymer solutions surface.

Fig. 6 - Krüss Tensiometer K9

Source: The picture taken by me

3.4.2. Conductivity:

The conductivities of solutions were measured by conductivity meter OK-102/1 branded Radelkis. Electrodes of the device are inserted into solution and conductivity values are displayed on the scale of the device.

Fig. 7 - Conductivity meter; OK-102/1, Radelkis.

Source: The picture taken by me

3.4.3. Zero shear viscosity:

In order to obtain viscosity behavior of solutions, chosen shear rate is from 10 s^{-1} to 6000 s^{-1} in linear scale at 23 ^{o}C. The result from this measurement gives us the behavior of viscosity under shearing. After measuring viscosity of solutions, there will have relations between concentration of solution and viscosity and their affect on Taylor cone number. Viscosity Meter, I have used is shown in fig.8.

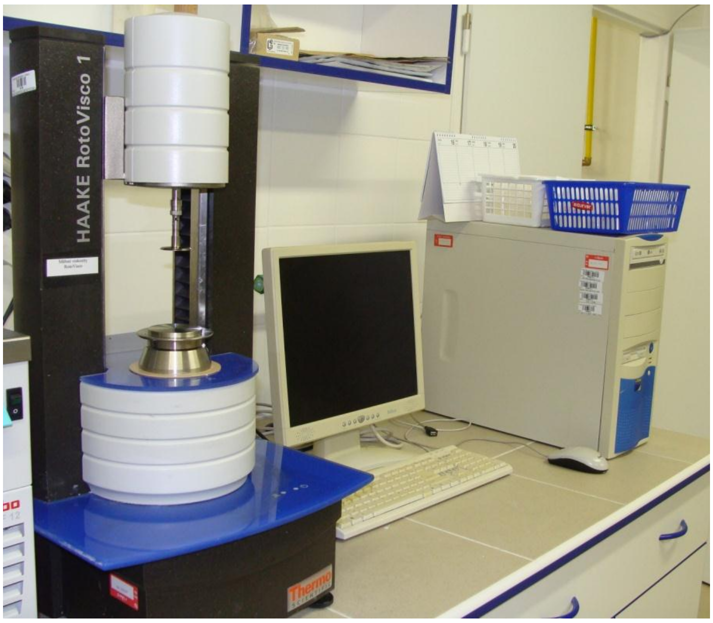

Fig. 8 - Viscosity meter brand Haake RotoVisco1

Source: The picture taken by me

3.4.4. Electrospinning Process:

After the measurements of polymer properties, solutions were taken to be spun to roller electrospinning device in the laboratory of Technical University of Liberec. Fig. 9 is the electrospinning device.

Fig. 9 - Roller spinning apparatus.

Source: The picture is taken by me

Required parameters for electrospinning process are shown in following table 4. According to previous experiments [Dao, A.T. (2009); Callioglu F.C. (2011)]

Table 4 - Setting parameters of needleless (roller) electrospinning

Roller length (cm)	14,5
Roller diameter (cm)	2
Roller angular velocity (rpm)	5
Distance between electrodes (cm)	18
Velocity of the running collector fabric (cm/min)	10
Applied voltage (kV)	60
Temperature (^{o}C)	17
Relative humidity (%)	25

Source: Data-my own, table- created by me

3.4.5. Current meter:

Since the beginning of the electrospinning process, current of the system carried on by polymer solution, was measured with the device branded Agilest, 34401A (Fig. 10).

Fig. 10 - Current measuring device

Source: The picture is taken by me

3.4.6. High Speed Camera:

Electrospinning process was done under record of high speed camera Sony Full HD brand, NEX-VG10E Handycam (14.2mp) series with E18-200mm lens. (Fig.11) The camera was placed in front of spinning machine and currentmeter was arranged to work simultaneously with the camera. The purpose of this record was to see the number of Taylor cones and time of cone formation while the current passing through polymer from roller to collector. Subsequently, records were analyzed, average number of Taylor cones were calculated and compared with current graphics.

Fig. 11 - Sony Full HD brand, NEX-VG10E Handycam - used to record electrospinning process.

Source:[sony(2012)]

3.4.7. SEM and Nis elements (Analyze of fibers):

After finishing electrospinning process, in order to see the existence of the nanofibers and elimination of non fibrous areas, Scanning Electron Microscope (SEM) Phenom FEI (Fig.12) was used to picture microstructure of nanofibers fabric (membrane). The properties of nanofibers membrane as fiber diameter and non-fibrous area were determined by using Nis-Elements picture analyze program.

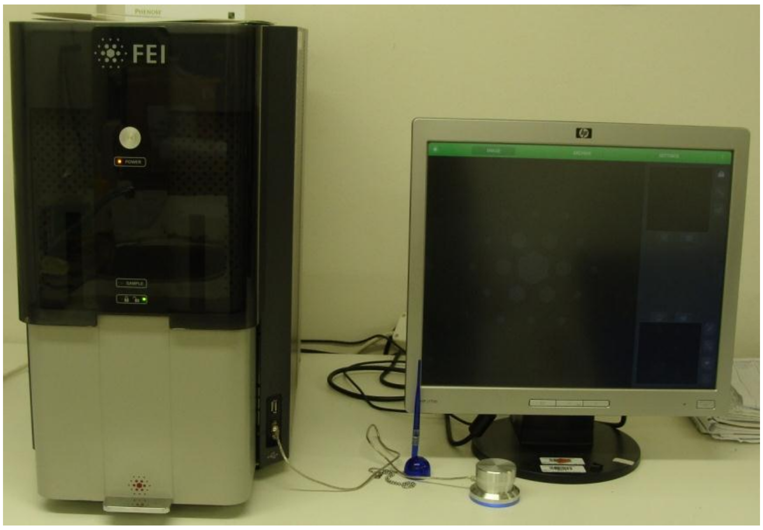

Fig. 12 - SEM- Phenom FEI

Source: The picture taken by me

Mean fiber diameters and distributions of fiber diameters for different solutions are investigated then relation between fiber diameter and current also relation between fiber diameter and concentration of Taylor cones were analyzed by Nis elements image analyzing program (Fig.13).

A) B)

Fig. 13 - Measurement of fiber diameter with nis-element A)SEM picture of nano membrane. B) Scene from Nis-elements.

Source:The pictures taken by me

4. RESULTS AND DICUSSION

During this chapter, result of the experiments will be explained. The results were shown in tables and in graphics. Results are including the independent and dependent properties of the solution. Results of independent parameters as surface tension, conductivity and zero shear viscosity, for easier comparison, will be demonstrated with weight concentration of polymer and weight concentration of salt. The dependent parameters of electrospinning process as throughput, number of Taylor cones, distance between neighboring Taylor cones, throughput per Taylor cone and current per Taylor cone will be shown so that some relations between dependent parameters-concentration of solutions, dependent parameters- concentration of salt in solution, current-throughput, and current per jet- throughput per jet will be described and illustrated in graphics.

4.1. PEO of various weight concentrations in solution:

4.1.1. The solutions' properties:

This part of work shows some independent properties of the PEO solution as zero shear viscosity, conductivity and surface tension (Table 5).

Table 5 - Properties of the PEO solutions:

Solution concentration [wt%]	Zero shear viscosity [Pas]	Conductivity [mS/cm]	Surface tension [mN/m]
3% PEO	0,059	0,128	57,8
4% PEO	0,115	0,248	63,7
4% PEO+0,1% NaCl	0,105	5,8	59,8
4% PEO+0,3% NaCl	0,107	16,2	56,2
4% PEO+0,5% NaCl	0,107	24,1	64,1
4% PEO+1% NaCl	0,104	41,8	52,8
4% PEO+1,5% NaCl	0,109	63	57,5
4% PEO+2% NaCl	0,111	71	37,9
5% PEO	0,151	0,25	59,8
5% PEO+0,1% NaCl	0,130	7,2	67,6
5% PEO+0,3% NaCl	0,150	10,4	67,8
5% PEO+0,5% NaCl	0,165	25,9	65,4
5% PEO+1% NaCl	0,167	43	68,5
5% PEO+1,5% NaCl	0,168	62	66,5
5% PEO+2% NaCl	0,163	84	68,2

Source: Data - measured by me, table - created by me

Based on date from table 5, the relationship between these independent properties and PEO polymer concentration is shown graphs form below.

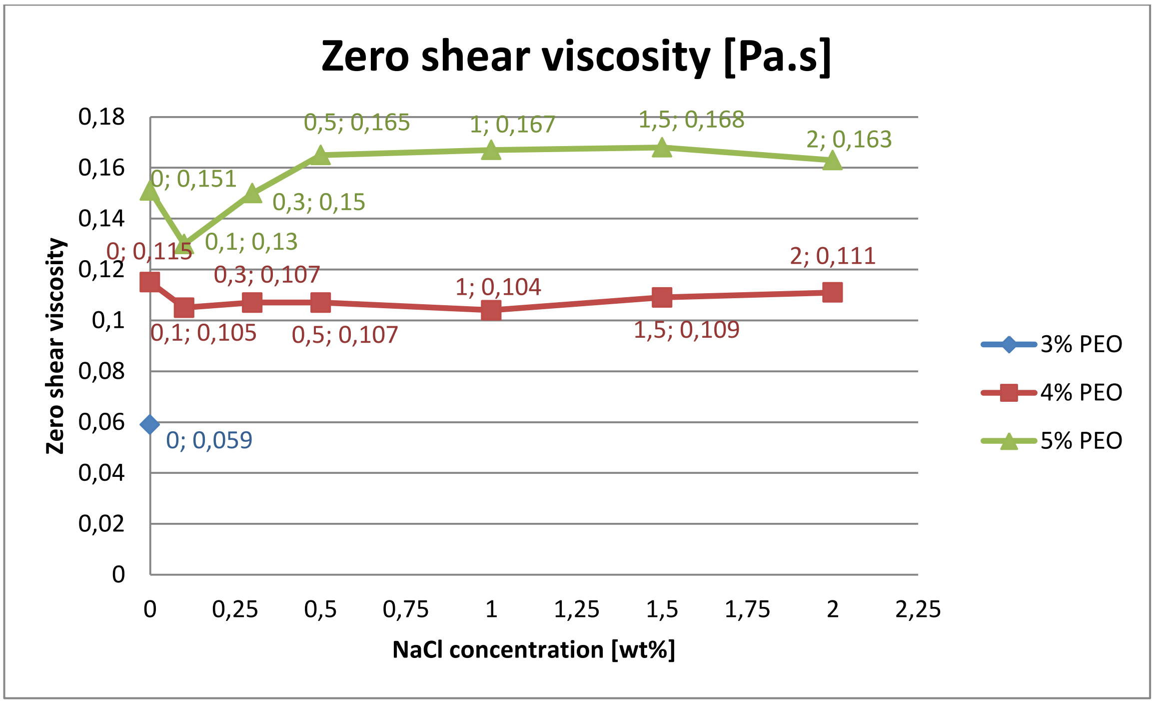

Fig. 14 - Comparison of zero shear viscosity.

Source: Data - measured by me, graph - own construction

Zero shear viscosity does not change with concentration of NaCl salt due to Poly (ethylene oxide)'s chemical structure:

$$-[CH_2\text{-}CH_2\text{-}O]_n-$$

This chain structure does not bond with NaCl salt ions, therefore viscosity of the solution has a linear course because of the main structure of the polymer chain does not change.

As it is seen from the graph, fig. 14, different concentrations of PEO have different viscosity due to its effect on the molecular weight of the polymer solution. Increasing of PEO concentration in solution, accordingly, increases the zero shear viscosity of the solution.

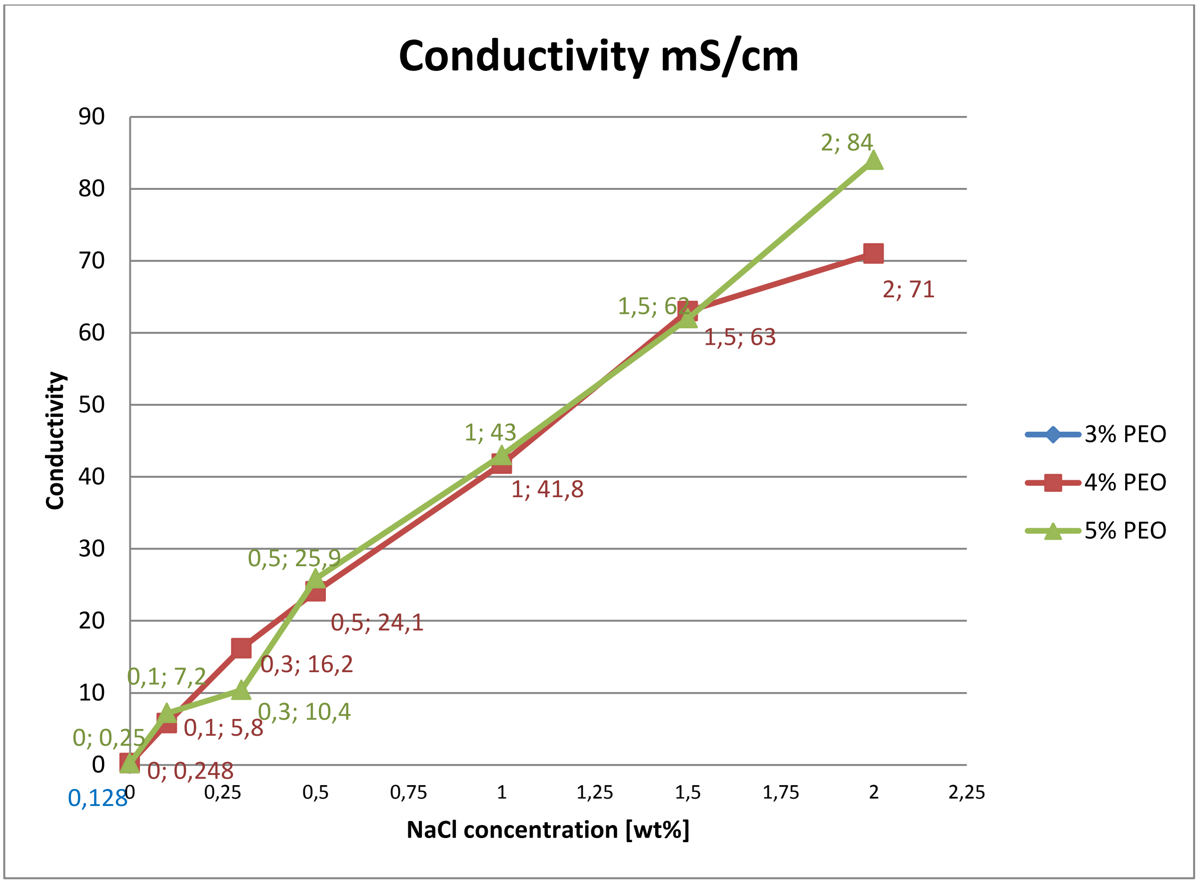

Fig. 15 - Dependence of conductivity on salt concentration

Source: Source: Data - measured by me, graph - own construction

Even though trend of conductivity seems linear, in fact affect of salt on conductivity is exponentially increasing (Fig. 15). NaCl salt dissolves in water solvent into Na^+ and Cl^- ions, which are carrier of conductivity, thus conductivity of the polymer solution increases. But at some point as solution goes closer to saturated state, increasing rate slows down because of excessive load of ions.

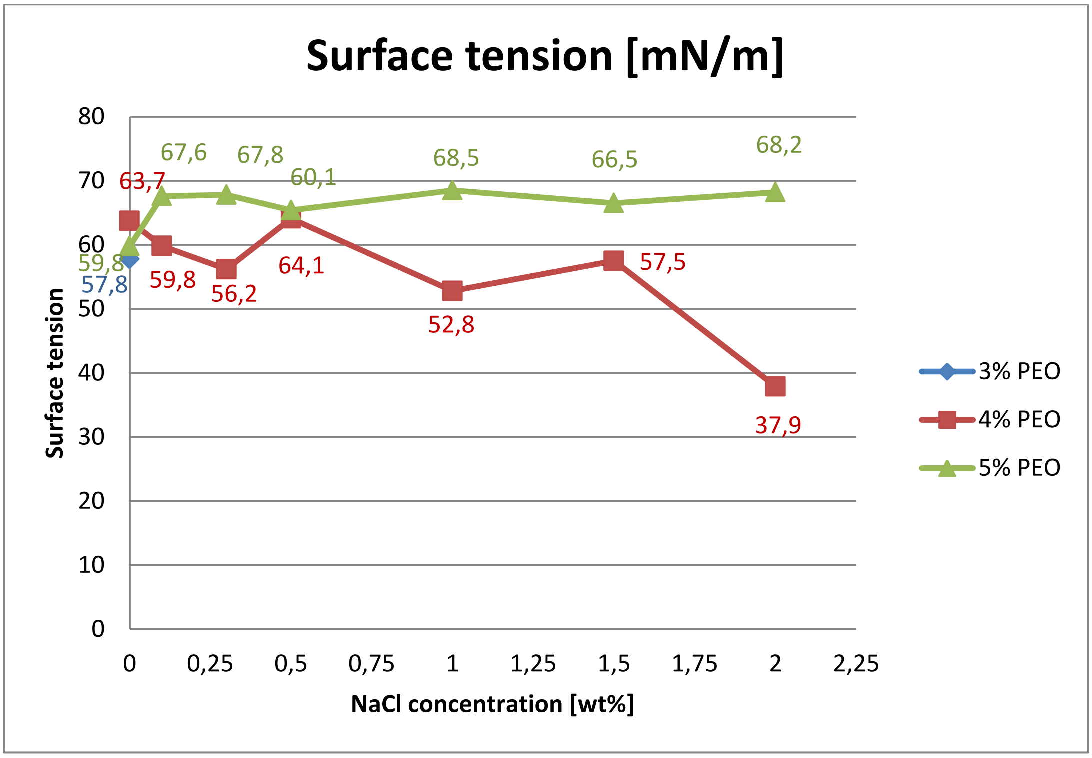

Fig. 16 - Dependence of surface tension on salt concentration

Source: Data - measured by me, graph - own construction

Dependence of surface tension on salt concentration behaves in similar way with zero shear viscosity (see Fig.14 and Fig.16) NaCl salt concentration does not show any significant affect on viscosity of solution.

Analyzing of independent parameters showed that behaves of different Poly (ethylene oxide) concentrated solutions are very similar under the effect of addition of various concentration of NaCl salt. Both surface tension and zero shear viscosity don't state any significant change on solutions' property when they have different NaCl salt concentration. However, in all solutions, conductivity of the solutions with different PEO concentrations increase as the NaCl concentration increases. All the solutions behave analogically. Henceforward, 4% PEO solution without NaCl will be taken into consideration along with 3% PEO without NaCl and 5% PEO without NaCl. In order to see the effect of salt on dependent parameters, different concentration of NaCl salt was added to only 5wt% PEO solution.

4.1.2. Dependent parameters:

This section shows the results of some dependent parameters include fiber diameter, polymer throughput and throughput per Taylor cone, average current and current per without NaCl salt will be investigated in order to help understanding comparison of affect of Polymer concentration. These parameters are related to process of electrospinning. Measurements are done during and after roller electrospinning process.

Table 6 - Dependent parameters of polymer solutions.

Polymer concentration [wt%]	Number of jets (N)	Mean Fiber diameter [µm]	Throughput (P) [g/min/m]	Throughput per Taylor cone (P/N)	Mean Current [mS/min]	Mean current per Taylor cone
3% PEO	79	-	-	-	99,1459	1,255011
4% PEO	81	-	-	-	208,8809	2,578777
5% PEO	100	-	-	-	261,8534	2,618534
5%PEO+0,1%NaCl	35	0,21	0,296	0,008457	184,4459	5,269884
5%PEO+0,3%NaCl	33	0,23	0,526	0,015939	160,7471	4,871125
5%PEO+0,5%NaCl	30	0,19	0,501	0,0167	365,8741	12,1958
5%PEO+1%NaCl	20	0,22	0,249	0,01245	261,5115	13,07557
5%PEO+1,5%NaCl	13	0,24	0,169	0,013	222,5456	17,11889
5%PEO+2%NaCl	11	0,25	0,119	0,010818	213,1221	19,37474

Source: Data – measured and calculated by me, table - own construction

Table 6 shows the transmission performances, such as current and throughput. Even though, all the polymer solutions were spinnable, 3% PEO, 4% PEO and 5% PEO solutions without NaCl salt did not accomplish nano fiber membrane. The electrospinning of these solutions resulted as the electro spraying without creating nano fibers. That is why fiber diameter and fabric throughput were not able to be observed. The hereafter, fabric throughput and fiber diameter of solutions 3%, 4% and 5% PEO without NaCl salt will be indicated zero (0) in the graphs.

Change in number of Taylor cones of solutions with different PEO concentration (Fig.17) and different NaCl salt concentration (Fig.18) are illustrated in graphics. As the polymer concentration and viscosity increases, number of Taylor cones are increasing where the NaCl salt concentration and conductivity increases, number of Taylor cones decrease.

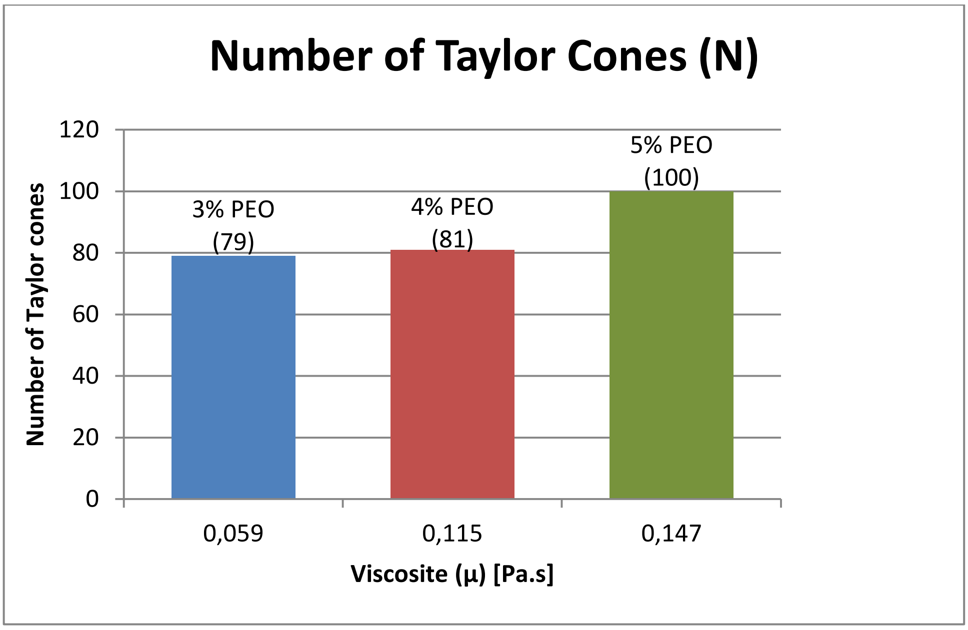

Fig. 17 - Number of Taylor cones of 3%, 4% and 5% PEO depend on viscosity.

Source: Data - measured by me, graph - own construction

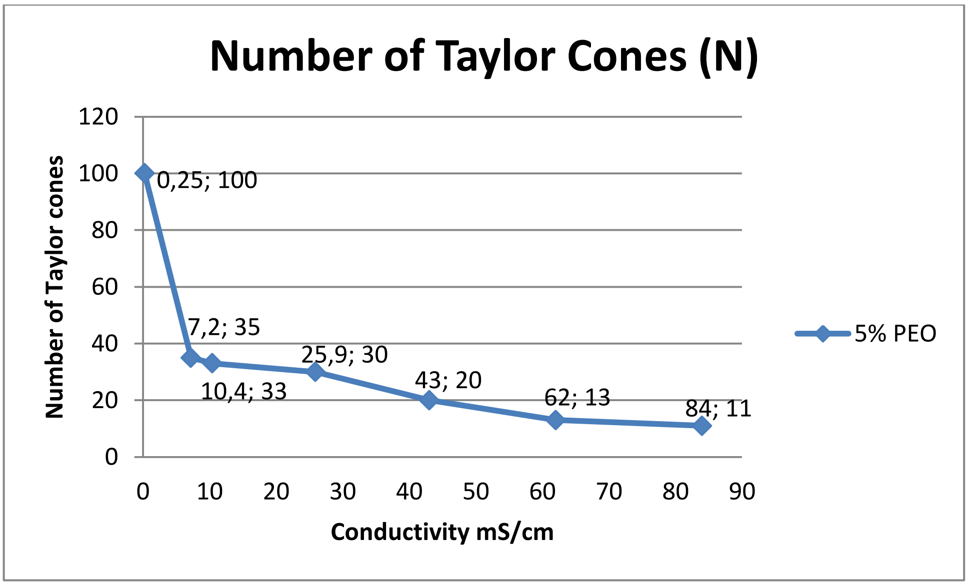

Fig. 18 - Number of Taylor cones of 5% PEO solution depended on conductivity

Source: Data - measured by me, graph - own construction

Diameter of fibers measured and table 7 shows the mean fiber diameters standard deviation, min and max diameter values.

Table 7 - Diameter of fibers with their standard deviation (σ)

	fiber diameters [µm]			
Polymer Solution	mean	st.dev.	min	max
5% PEO	0	0	0	0
5% PEO+0,1% NaCl	0,21	0,05	0,11	0,30
5% PEO+0,3% NaCl	0,23	0,06	0,10	0,37
5% PEO+0,5% NaCl	0,19	0,04	0,10	0,31
5% PEO+1% NaCl	0,22	0,04	0,13	0,35
5% PEO+1,5% NaCl	0,24	0,06	0,11	0,39
5% PEO+2% NaCl	0,25	0,05	0,14	0,37

Source: Data - measured by me, table - created by me

The graph below (Fig. 19) shows the fiber diameters of solutions with different conductivities. Error bars are representing standard deviation of fiber diameters. If error bars are taken into consideration, it is visible that change of diameter of fibers dependent on conductivity isn't significant.

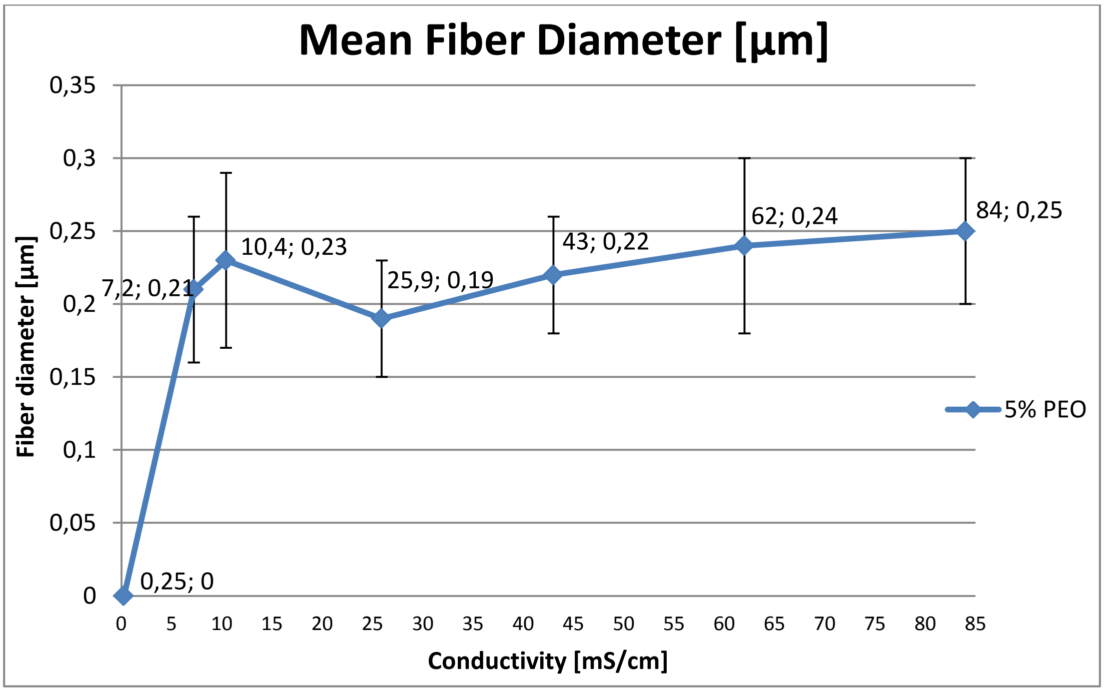

Fig. 19 - Changes of nano fiber diameters dependent on conductivity.

Source: Data - measured by me, graph - own construction

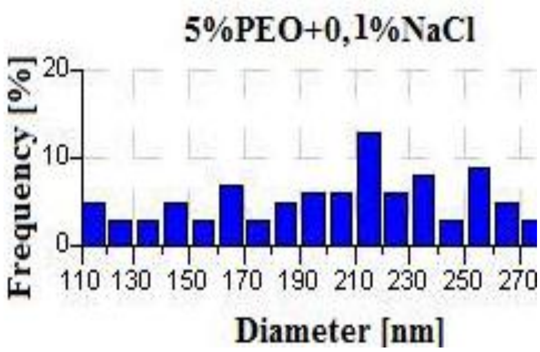

Fig. 20 - Diameter distribution of
5%PEO+0,1%NaCl

Source: Data- measured by me, Graph – created by Nis-elements

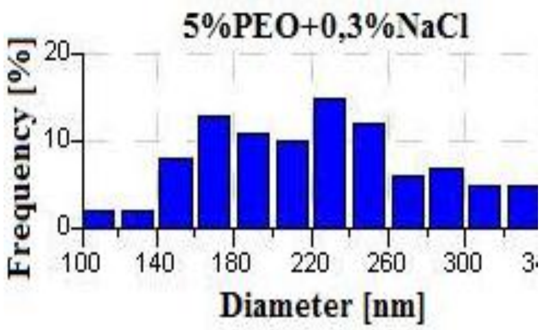

Fig. 21 - Diameter distribution of
5%PEO+0,3%NaCl

Source: Data- measured by me, Graph – created by Nis-elements

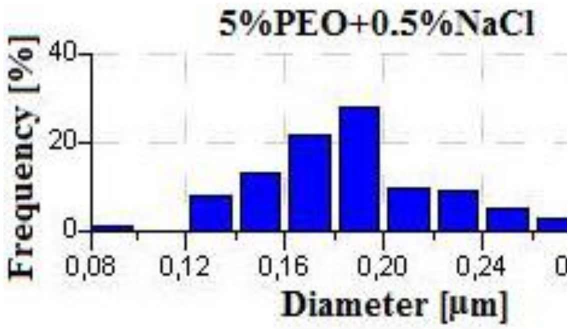

Fig. 22 - Diameter distribution of
5%PEO+0,5%NaCl

Source: Data- measured by me, Graph – created by Nis-elements

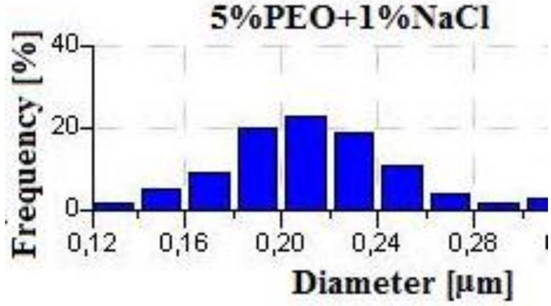

Fig. 23- Diameter distribution of
5%PEO+1%NaCl

Source: Data- measured by me, Graph – created by Nis-elements

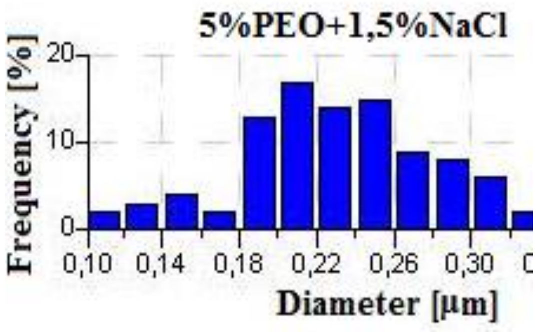

Fig. 24 - Diameter distribution of
5%PEO+1,5%NaCl

Source: Data- measured by me, Graph – created by Nis-elements

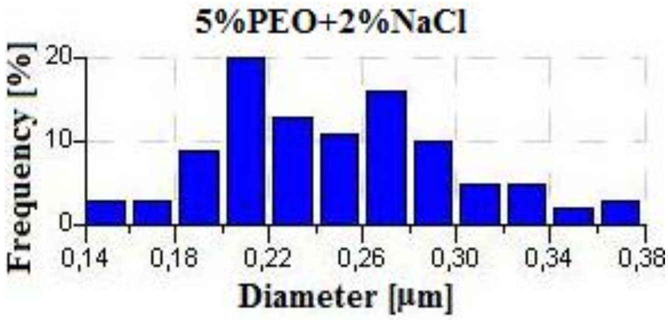

Fig. 25 - Diameter distribution of
5%PEO+2%NaCl

Source: Data- measured by me, Graph – created by Nis-elements

Distribution of fiber diameters are shown in the flowing graphs (Fig. 20-25). Conductivity which comes with NaCl salt, regulate the fiber distribution, and diameter of fibers represented with near normal distribution. Diameter of fibers of low conductive solution 5%PEO+0,1%NaCl is randomly distributed.

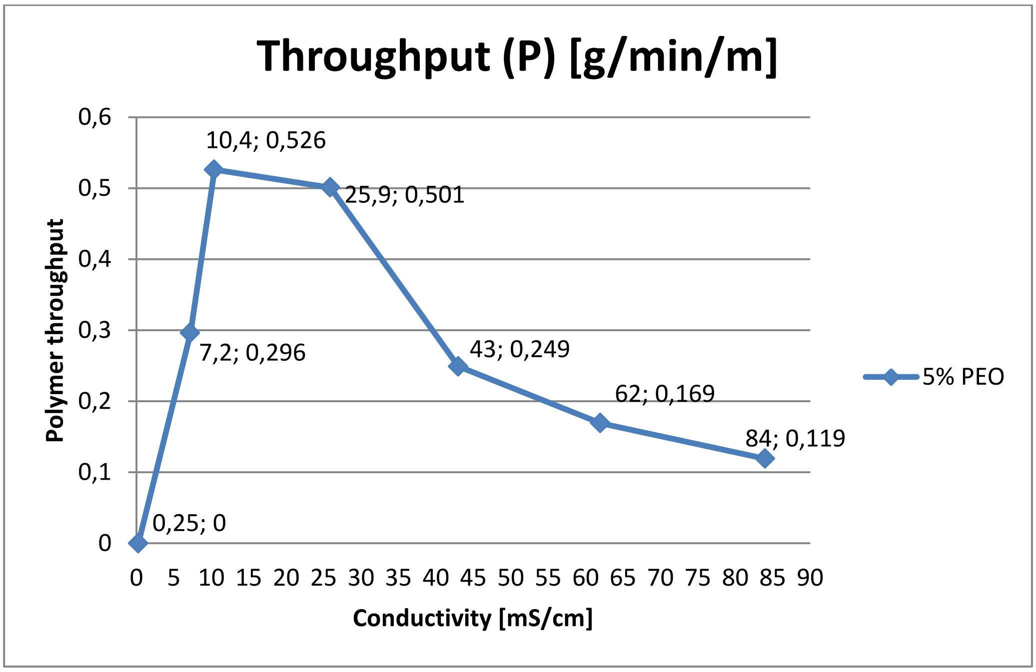

Fig. 26 - Polymer throughput of 5% PEO dependent on different conductivity levels

Source: Data- measured by me, Graph – own construction

From the graph (fig.26) that is seen throughput level is lowering down as the conductivity of the solution is increasing. Explanation of low value of the second point (7,2;0,296) is, throughput wasn't able be taken from whole collected nano fiber membrane due to electro spraying. On the places of electrospraying throughput wasn't measurable. However, throughput per Taylor cone wasn't changing significantly with different conductivities. Graph of it is following (Fig. 27).

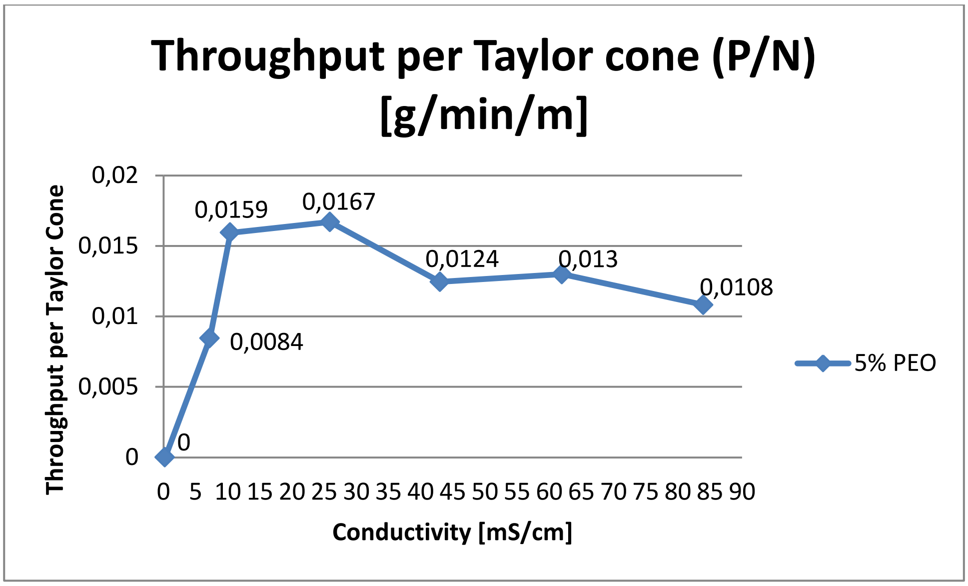

Fig. 27 - Polymer throughput of 5% PEO per one Taylor cone, dependent on different conductivity levels

Source: Data- measured by me, Graph – own construction

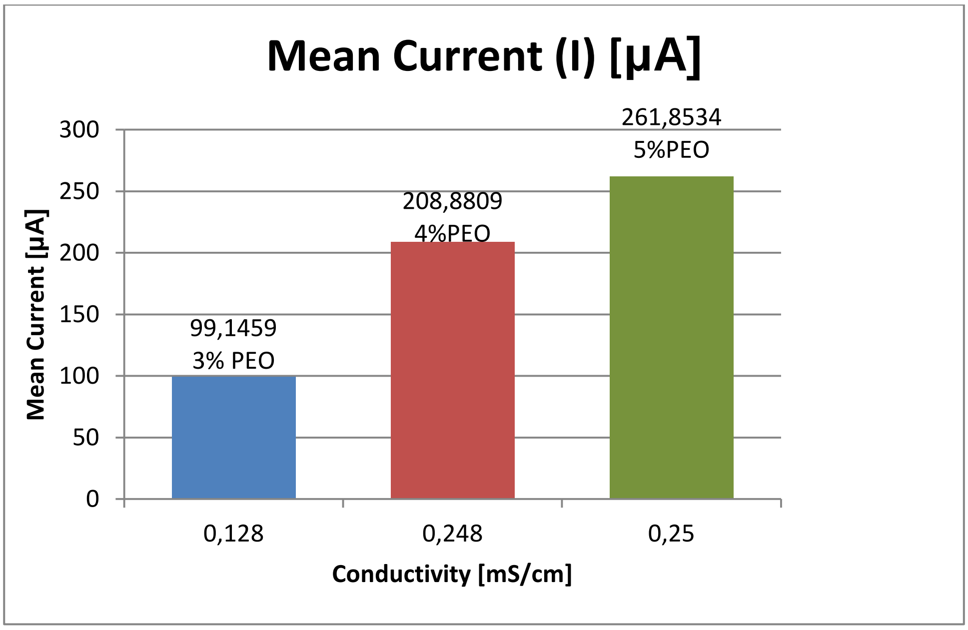

Fig. 28 - Comparison between mean current and conductivity, dependent on the polymer concentration.

Source: Data- measured by me, Graph – own construction

Mean current is increasing as the PEO concentration increases (Fig.28). It can be stated, from the formula of current I=U/R, resistance of polymer solution is greater whereas the polymer concentration is smaller.

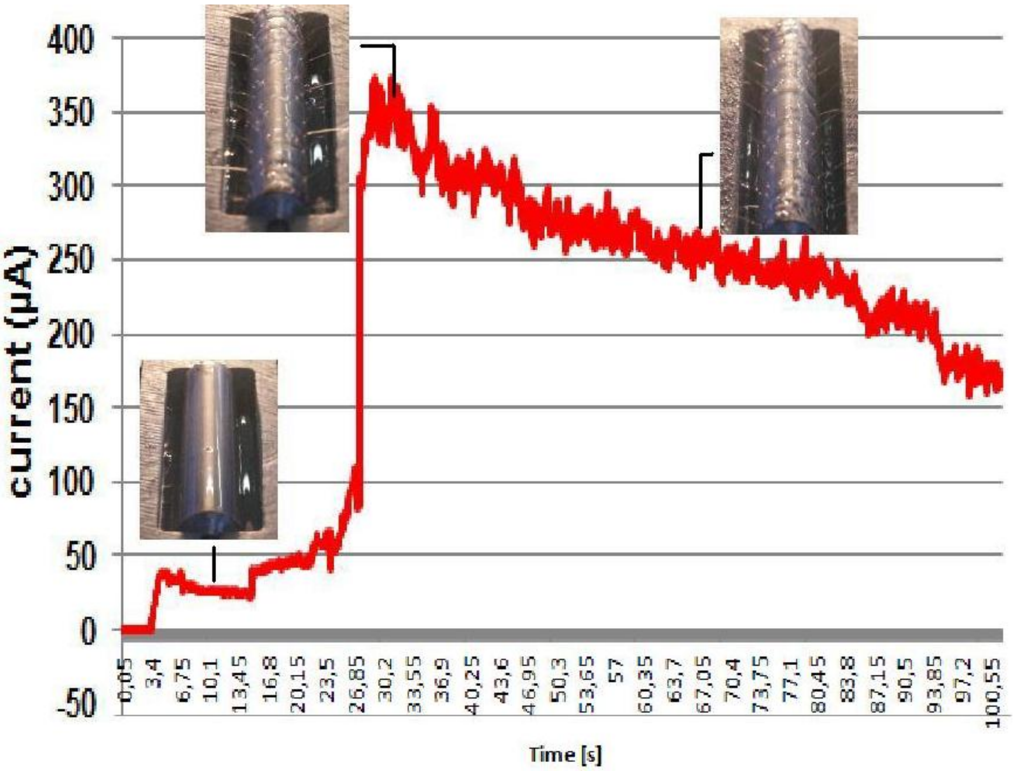

Fig. 29 - Current measurement in same time of Taylor cone formation

Source: Data- measured by me, Graph – own construction

From the figure 29 it is possible to see measured current values during formation of Taylor cones. Number of Taylor cones and the current of process don't show extreme change during the process of electrospinning. For illustration of number of Taylor cones at the 30th second and the 70th second are added to graph as picture of spinning roller. From the pictures it is possible to see numbers of Taylor cones are identical.

Following graphs (Fig. 30-36) show the change of current during electrospinning process of 5%PEO solutions with different concentrations of NaCl salt. From these graphs, it is seen that current of the process doesn't change during the process. Number of Taylor cones stay identically during whole process.

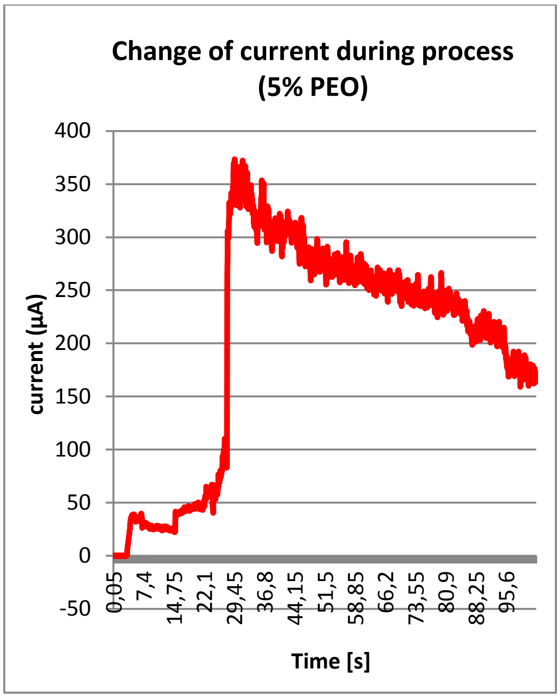

Fig. 30 - 5% PEO current change, during electrospinning

Source: Data- measured by me, Graph – own construction

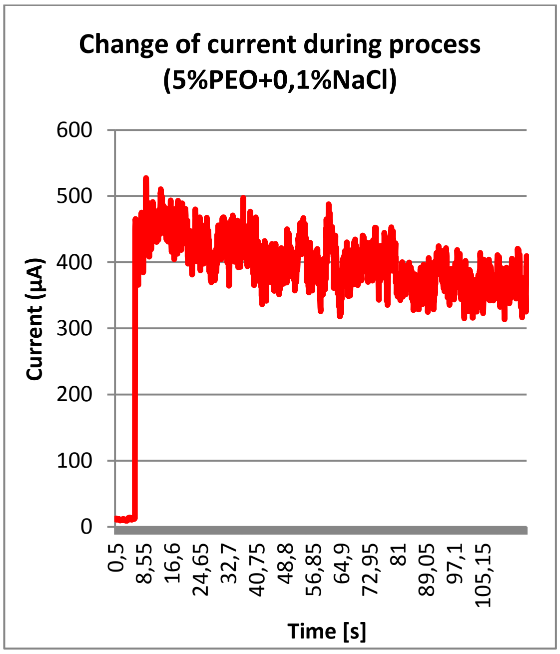

Fig. 31- 5%PEO+0,1%NaCl current change, during electrospinning

Source: Data- measured by me, Graph – own construction

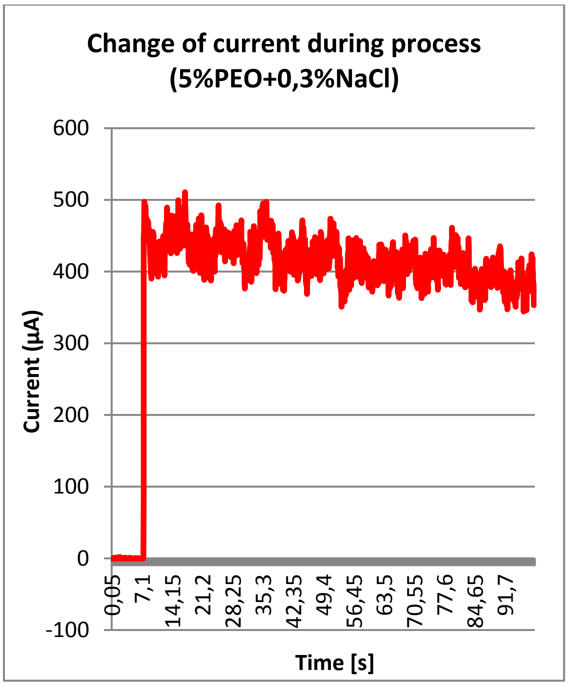

Fig. 32 - 5%PEO+0,3%NaCl current change, during electrospinning

Source: Data- measured by me, Graph – own construction

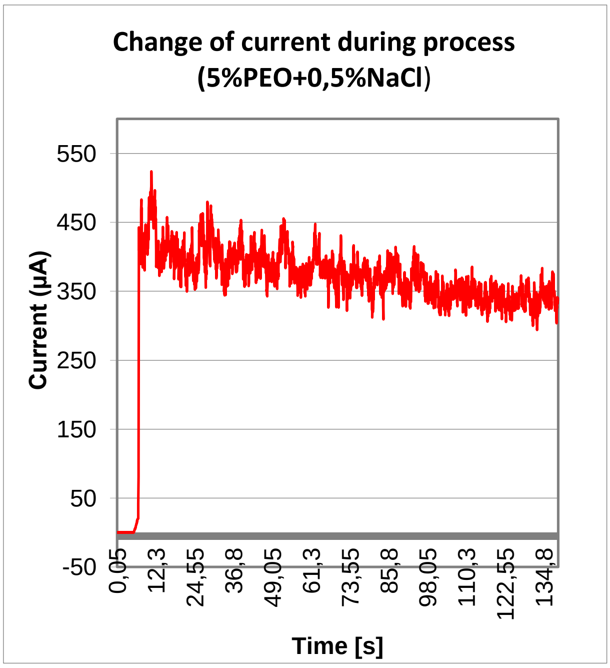

Fig. 33 - 5%PEO+0,5%NaCl current change, during electrospinning

Source: Data- measured by me, Graph – own construction

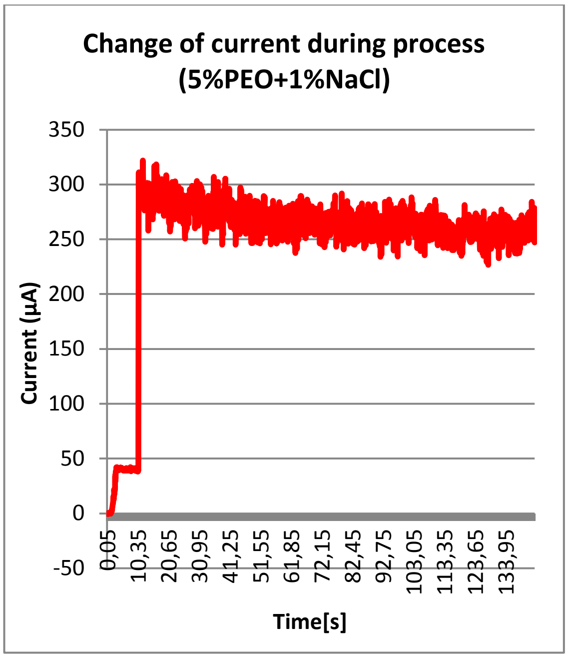

Fig. 34 - 5%PEO+1%NaCl current change, during electrospinning

Source: Data- measured by me, Graph – own construction

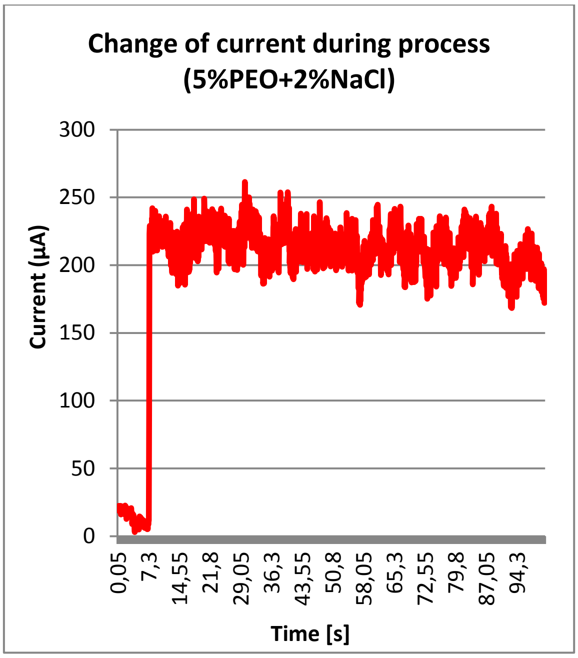

Fig. 36 - 5%PEO+2%NaCl current change, during electrospinning

Source: Data- measured by me, Graph – own construction

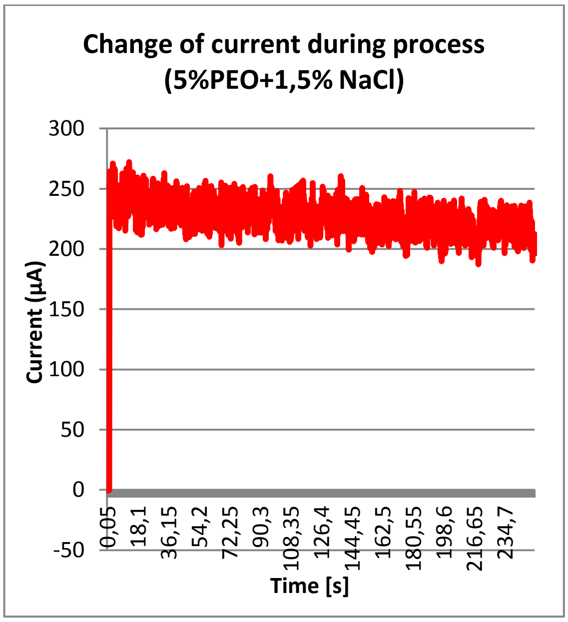

Fig. 35 - 5%PEO+1,5% NaCl current change, during electrospinning

Source: Data- measured by me, Graph – own construction

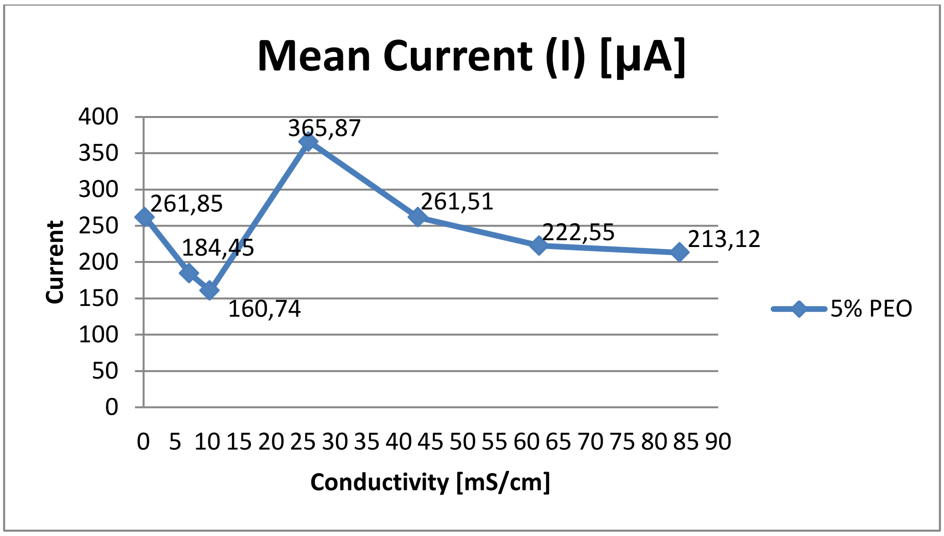

Fig. 37 - Current change of 5%PEO solution dependent on conductivity.

Source: Data- measured by me, Graph – own construction

Mean current is shown on the Fig. 37 above. According to this graph, mean current first decreases and then increases along with increase of polymer solution conductivity. But the changes aren't exaggerated that is why we can say change of current isn't highly dependent on conductivity. Number of Taylor cones have a great drop while the current is dropping from 261,85 μA to 184,45 and 160,74 during these processed it is observed that number of Taylor cones decreased from 100 to 30. When the NaCl salt concentration came to the some point (0,5%NaCl) and increase the conductivity (from 10,4 to 25,9 mS/cm) as 250% but when we look at the number of Taylor cones solution with 0,3% NaCl salt is 33 and solution with 0,5% NaCl salt is 30 which are so closed values. High effect of conductivity is the reason of this high increasing of current at 5% PEO+0,5% NaCl solution. Solution with 1% NaCl has 66% higher conductivity and 33% lower number of jets than the solution with 0,5 % NaCl. That means number of jets are has more affect on current than conductivity. Also solutions with 1,5% NaCl and with 2% NaCl presents lower Taylor cone number which reduces the average current.

$$I_{total} \sim E\ Q^{0,5} \kappa^{0,4}$$

Equation 9 – Equation of total current

Where I is total current, E is voltage, Q is feed rate and κ is solution conductivity [Shin et al. (2001)].

This equation is mainly valid for needle electrospinning but to understand the affect of conductivity on current it can be referred here. Feed rate (Q) can be considered analogous to number of jets. As it is seen, affect of feed rate (number of jets) is more than affects of the conductivity on the current.

However the graph follows (Fig. 38) shows the mean current per each Taylor cone. It is seen the drop of number of Taylor cones caused that each Taylor cone had to carry increased current as the conductivity of solution increased.

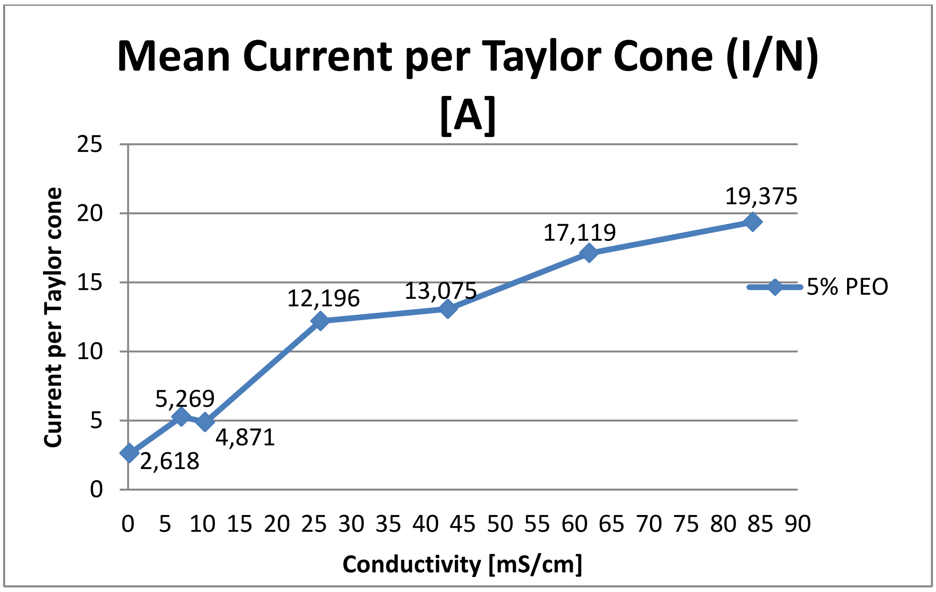

Fig. 38 - Mean current per Taylor Cone

Source: Data- measured by me, Graph – own construction

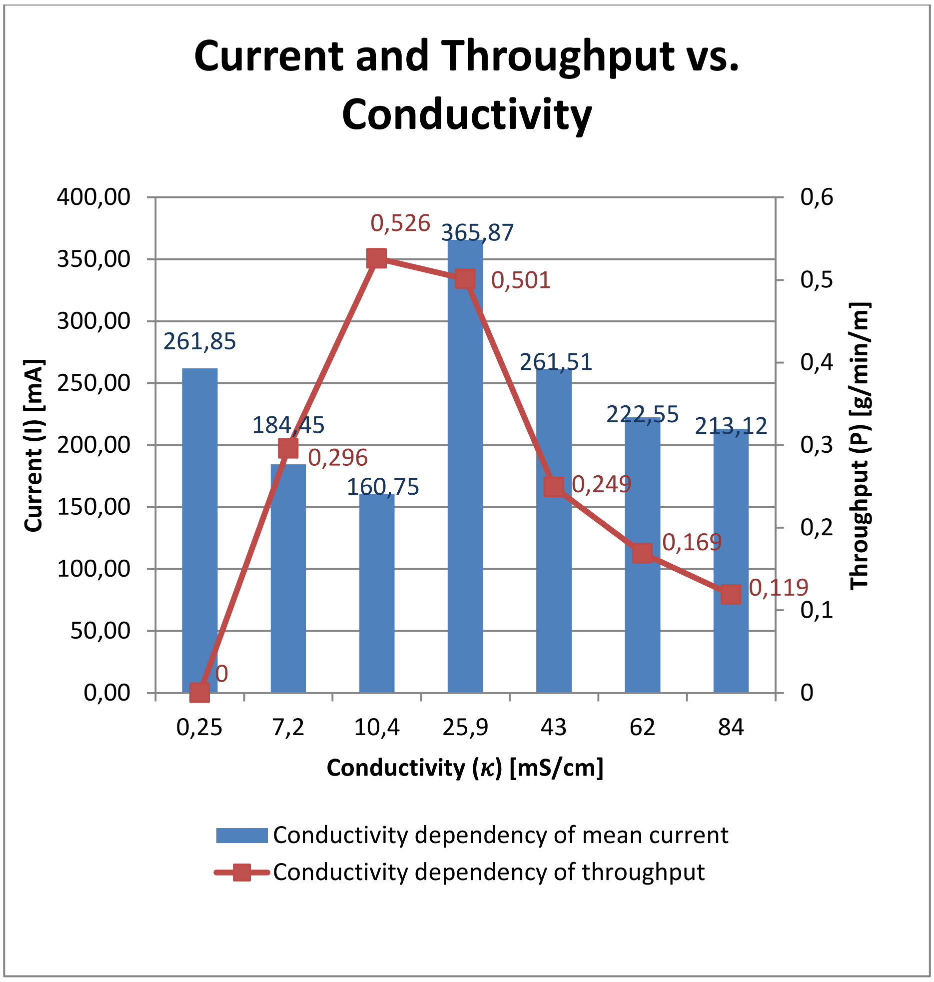

Fig. 39 – Current and throughput vs. conductivity

Source: Data- measured by me, Graph – own construction

The comparison of electrical current and polymer throughput with conductivity is shown in the fig.39. According to this graph maximum throughput was reached with minimum mean electrical current. While the conductivity of the polymer solution increases, throughput firstly rising and then slowly decreasing.

When the number of Taylor cones are getting less, carried current by Taylor cone is also getting less.

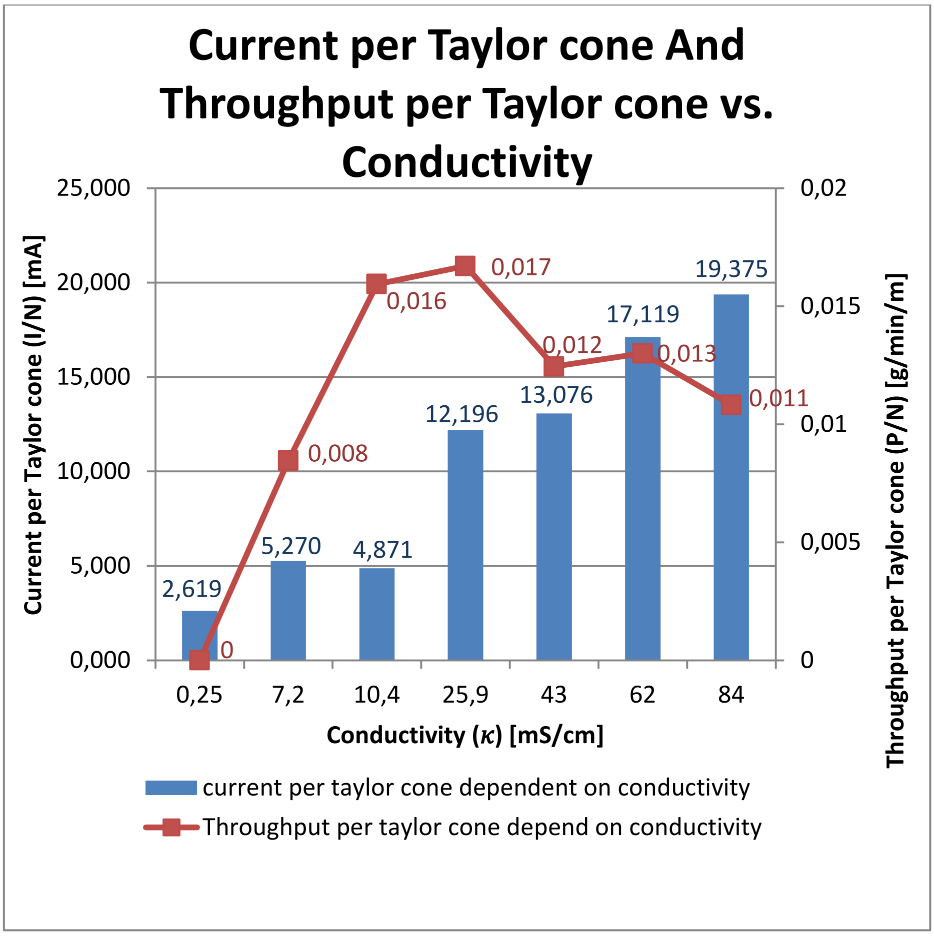

Fig. 40 – Current per Taylor cone and throughput per Taylor cone vs. Conductivity

Source: Data- measured by me, Graph – own construction

Augmentation of conductivity allows that one Taylor cone can carry more of current value. Fabric production from less number of Taylor cones isn't effective. That is why drop of throughput is seen with the increase of conductivity. Fig. 40 shows the change of throughput and current per Taylor cone with change of conductivity. It is possible to see after one point (0,3wt% NaCl, 10,4 mS/cm conductivity), the current per Taylor cone and throughput per Taylor cone don't have significant change while the conductivity gets higher.

4.2. Number of Taylor Cones per real spinning area (Concentration of Taylor cones) and Distance between Taylor Cones:

In many literatures, it is mentioned that theoretical spinning area A is considered to be approximately equal to one third of the spinning roller electrode (Equation 10):

$$A = \frac{1}{3} * \pi * r^2 * l$$

Equation 10 – Theoretical spinning area

From this formula theoretical spinning area of spinning roller that I used for my experiment is found as:

$$A = \frac{1}{3} * \pi * 2^2 * 14{,}5$$

$$A = 60{,}73746$$

Spinning area A is composed of n is the number of imaginary identical squares which is surrounding one Taylor cones[3].

$$A = n * x^2$$

Where n is the number of Taylor cones on the spinning area *A* and *x* is length of the square side (and the distance between Taylor cones simultaneously)

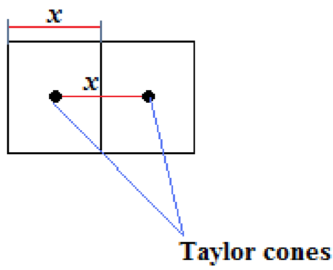

Fig. 41 – Distance between Taylor cones

Source: [Yener et al. (to be published)], Scheme – own construction

From the schematic explanation (Fig.14), the average distance *x* between adjoining Taylor cones is then [Yener et al. (to be published)]:

[3] However, Number of identical squares (n)=Number of Taylor cones (N_c)

$$x = \sqrt{\frac{A}{n}}$$

Equation 11- Equation of average distance between adjoining Taylor cones

Density of Taylor cones are calculated with the following formula equation 12.

$$D = \frac{N_c}{A}$$

Equation 12 – Equation of density of Taylor cones

Table.7 shows distance between Taylor cones, area of spinning and density of Taylor cones.

Table 8 - Taylor cone concentration

Polymer concentration [wt%]	Number of Taylor cones (N)	Spinning area (A) [cm^2]	Mean distance between Taylor cones (x) [cm]	Density of Taylor cones (N/A) [cm^{-2}]
3% PEO	79	60,73746	0,876829	1,30068
4% PEO	81	60,73746	0,865936	1,333609
5% PEO	100	60,73746	0,779342	1,64643
5% PEO + 0,1%NaCl	35	60,73746	1,317329	0,576251
5% PEO + 0,3%NaCl	33	56,52279	1,308744	0,583835
5% PEO + 0,5%NaCl	30	60,73746	1,422878	0,493929
5% PEO + 1%NaCl	20	53,29873	1,632463	0,375243
5% PEO + 1,5%NaCl	13	51,19376	1,984435	0,253937
5% PEO + 2%NaCl	11	30,36873	1,661564	0,362215

Source: Data- measured and calculated by me, Table – own construction

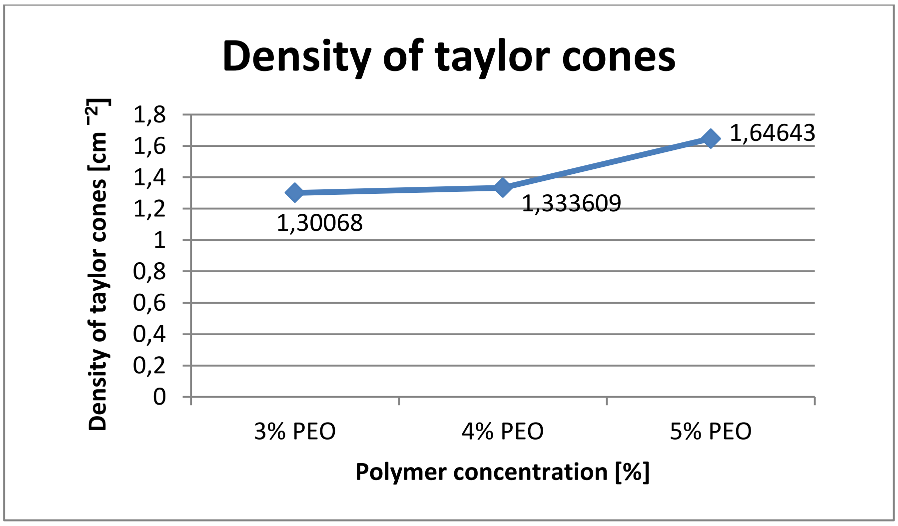

Fig. 42 – Density of Taylor cones

Source: Data- calculated by me, Graph – own construction

Densities of Taylor cones have increasing rate as the polymer concentration increases.(Fig.42) Spinning area on the roller is in the maximum value (one third of roller surface area) during spinning process with the solution without NaCl salt.

Density (concentration) of Taylor cones is negatively affected by NaCl salt concentration. Fig. 43 shows the concentration of Taylor cones with different NaCl salt concentrations. Here is possible to see density of Taylor cones are decreasing where as the concentration of NaCl salt and conductivity increases.

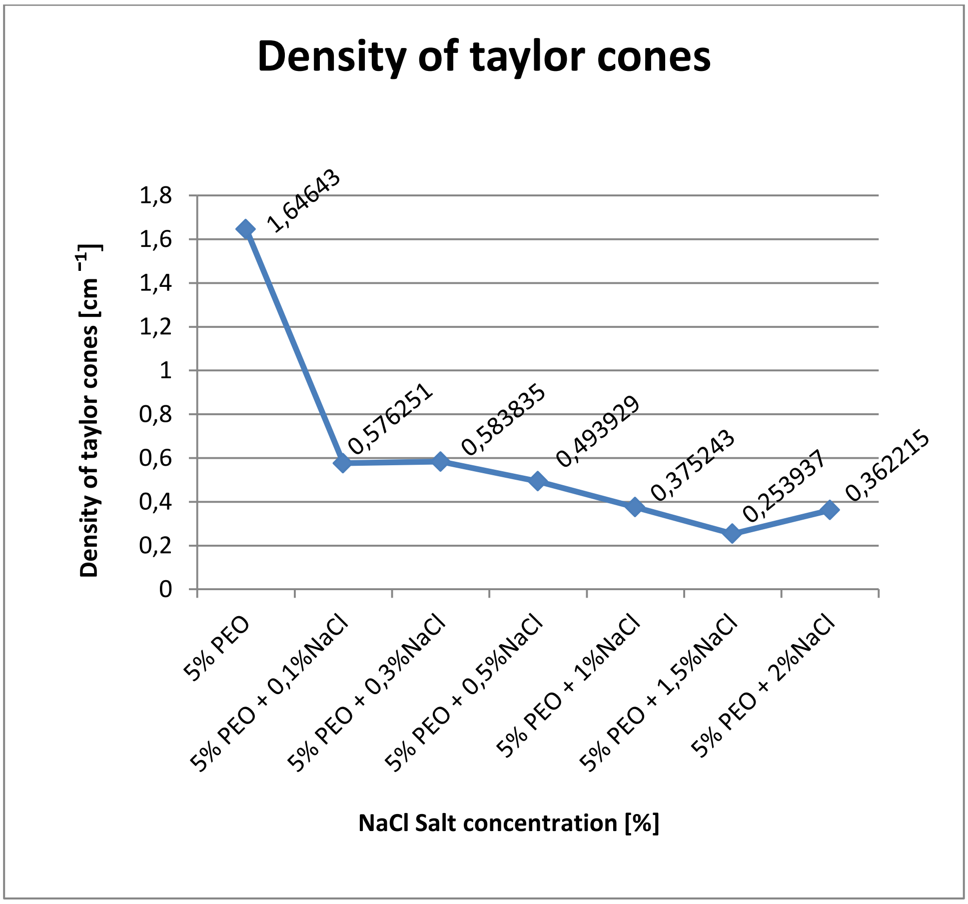

Fig. 43 – Density of Taylor cones

Source: Data- calculated by me, Graph – own construction

Diminish of density of Taylor cones is a reason to have low polymer throughput while adding the NaCl salt to the solution. Lower number of Taylor cones is caring out less amount of polymer solution that is why creation of nanofibers web slows down. Productivity of the process is lessened with higher conductivity and lower Taylor cone during the experiment.

Number of Taylor cones and concentration of Taylor cones are very identical under same conductivity (Fig.44). Where there is less number of Taylor cones, area of spinning is less too that is why concentration of Taylor cones is showing the variation just as number of Taylor cones.

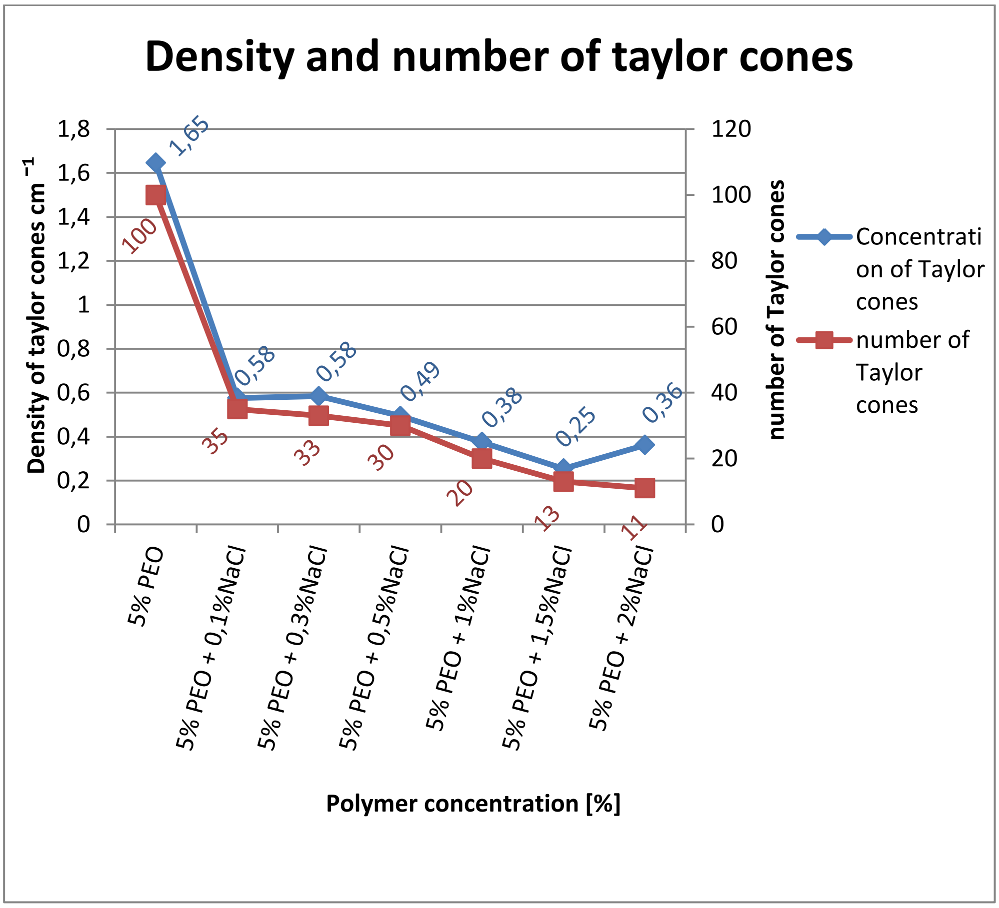

Fig. 44 - Density and number of cones

Source: Data- measured by me, Graph – own construction

Concentrations of Taylor cones don't show any extreme change. Density of Taylor cones three times bigger when there isn't any addition of NaCl salt than the solution with various NaCl salt concentrations. Different NaCl salt concentration still shows (Fig. 45) very similar density of Taylor cones. From this, it is possible to say density of Taylor cones doesn't significantly affect the productivity of electrospinning process.

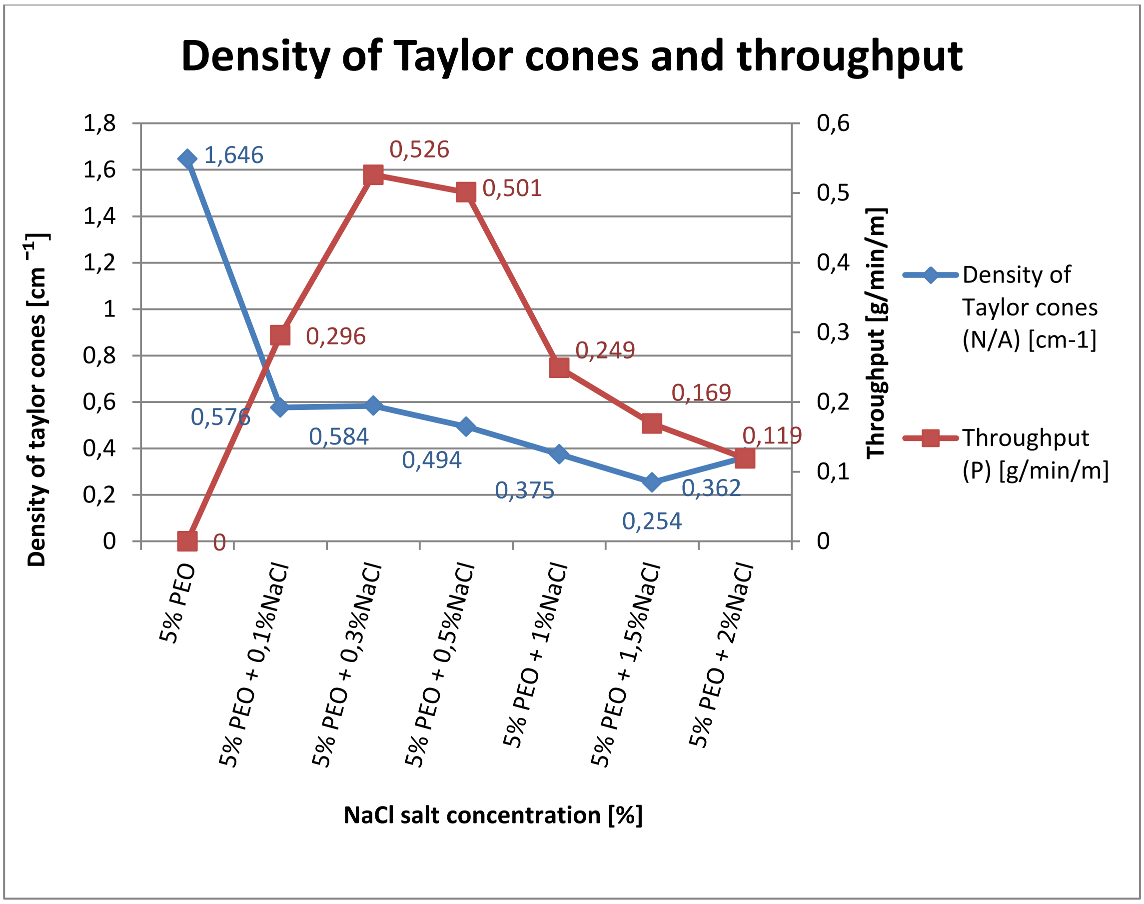

Fig. 45 – Density of Taylor cones and throughput

Source: Data- measured by me, Graph – own construction

5. CONCLUSION

Needleless electrospinning is a technique using electrical forces to tear and push spinning jets from free surface liquid toward electrode collector. This work uses the apparatus based needleless technique to produce nanofibers membrane.

There are two main groups of scientific contribution done in this thesis: the first contribution is definitions of process parameters and methods to measure the parameters in needleless electrospinning; the second one is the experimental study and explanation of relationships between some selected parameters. These scientific contributions are presented below.

The studies above have stated out definitions and methods to measure the independent and dependent parameters in needleless electrospinning technique. Some completely new parameters in needleless electrospinning such as throughput, density of cones, throughput per cone, non-fibrous area have been described, defined and methods to measure the parameters were developed.

From literature, it is seen that polymer molecular weight, concentration of solution and additives have a big role on some dependent parameters such as throughput, number of Taylor cones, concentration of Taylor cones and fiber diameters. The results of experiments show that throughput and mean current increase with increasing polymer concentration in solution. However number of Taylor cones increases with increasing polymer concentration; nevertheless, it decreases with increasing of NaCl salt concentration.

Zero shear viscosity and surface tension aren't affected where the conductivity of polymer solution increases with increasing of NaCl salt concentration. However, zero shear viscosity increases with increasing of the polymer PEO concentration and conductivity increases slightly as well.

As electrospinning device first starts, current of the system is near zero, after the formation of first Taylor cone, current of the system jumps to 200μA up to 500μA and the current value is stabilized. There for number of Taylor cones stays stable for each polymer solution.

Conductivity of spinning solution affects strongly needleless electrospinning dependent parameters, especially the throughput and density of cones. On the contrary, it almost does not affect the throughput per cone. Throughput per Taylor cone doesn't show any significant change while the conductivity of the solution changes. Throughput parameter and density of cones decrease strongly with increasing conductivity of spinning solution. It is a phenomenon to be explained by physicist and other experiments. Described experimental results are not sufficient to work out such explanation.

Contrary to theory, real spinning area was found out by using image analyzing that may be smaller than one third of roller surface area. That fact effects the concentration of Taylor cones. However, density of Taylor cones, spinning area and throughput values decrease synchronize.

This thesis is an initiative work, which is concentrated on electrical current, concentration of Taylor cones and polymer throughput. In future, I suggest, studies continue with focusing on full understanding of relations between current, Taylor cone and throughput. Throughput can be predicted from the concentration of Taylor cone at the needleless electrospinning. This research can be done under changing conditions to see the affects of independent parameters.

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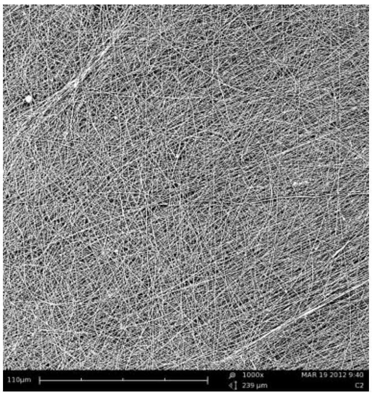
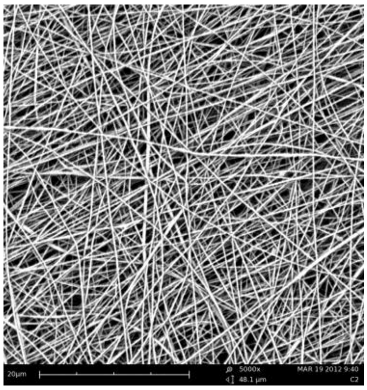
APPENDIX

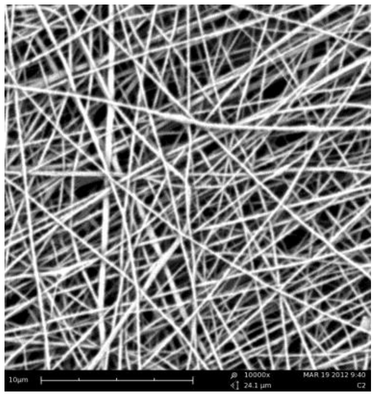
SEM images of nano fibers with NaCl salt (various concentrations of NaCl)



5%PEO+0,1%NaCl (SEM 1000x)



5%PEO+0,1%NaCl (SEM 5000x)



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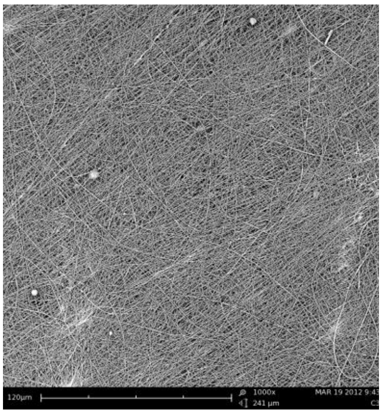

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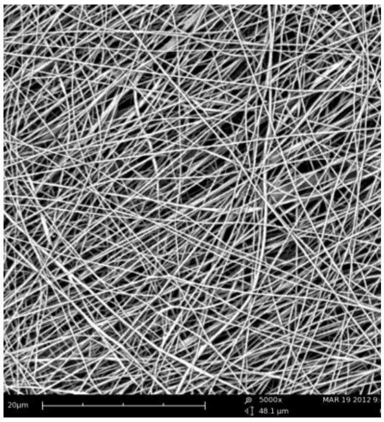
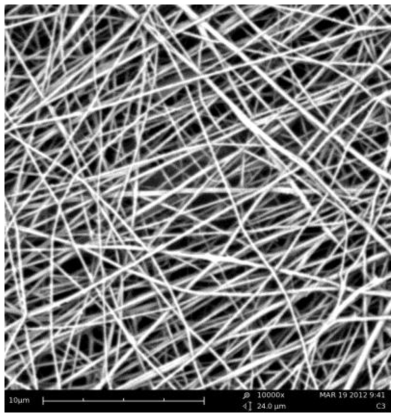
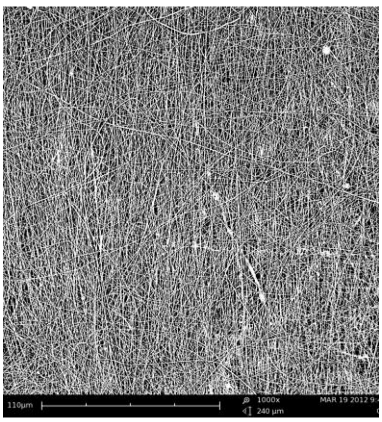


5%PEO+0,3%NaCl (SEM 5000x)



5%PEO+0,3%NaCl (SEM 10000x)



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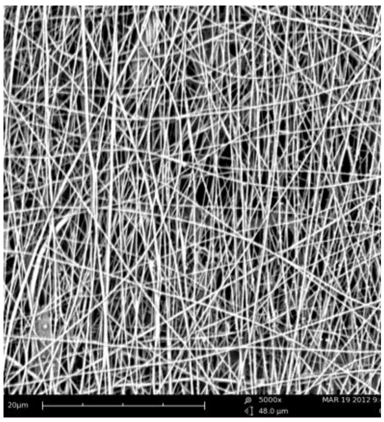

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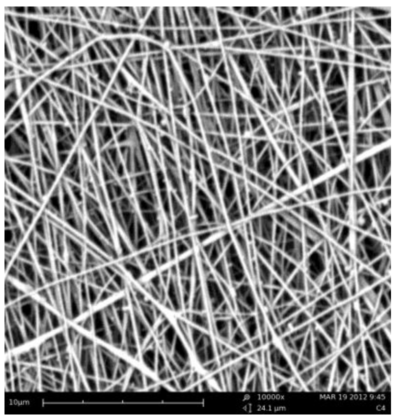
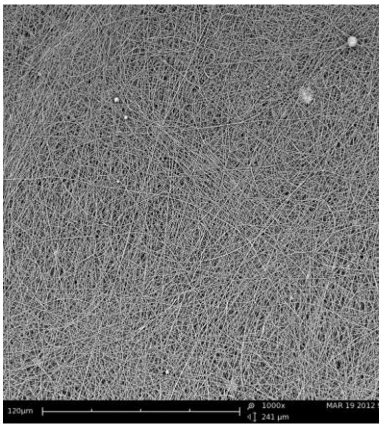
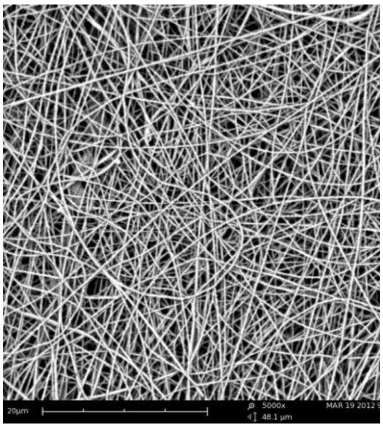


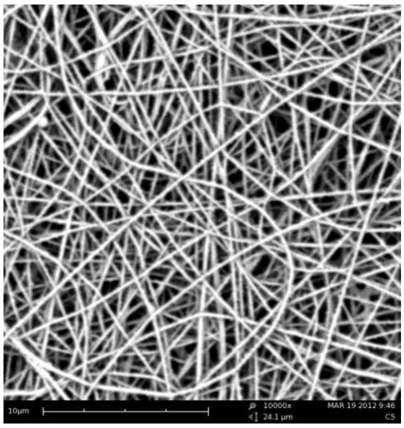
5%PEO+0,1%NaCl (SEM 10000x)



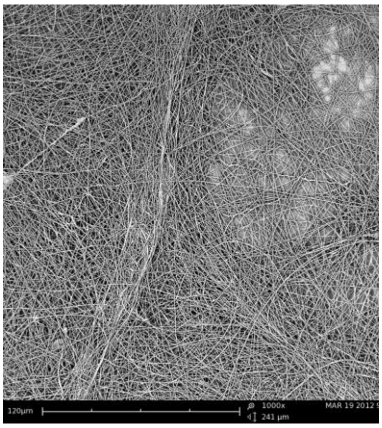
5%PEO+1%NaCl (SEM 1000x)



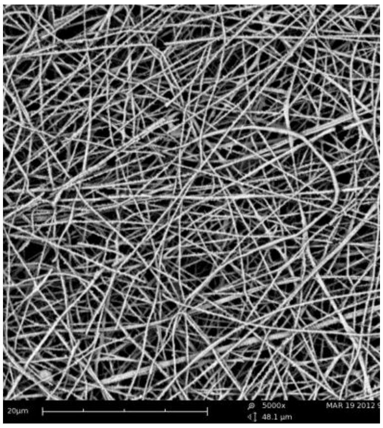
5%PEO+1%NaCl (SEM 5000x)



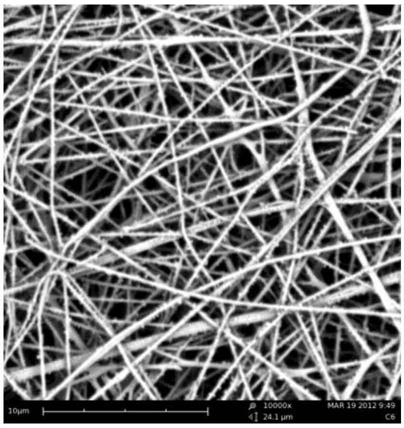
5%PEO+1%NaCl (SEM 10000x)



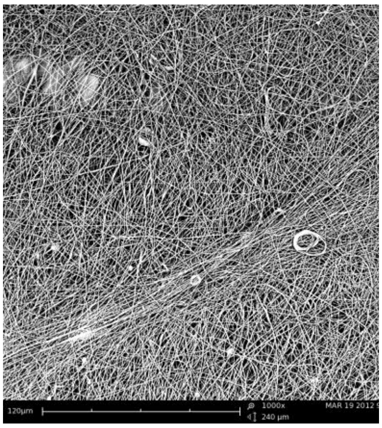
5%PEO+1,5%NaCl (SEM 1000x)



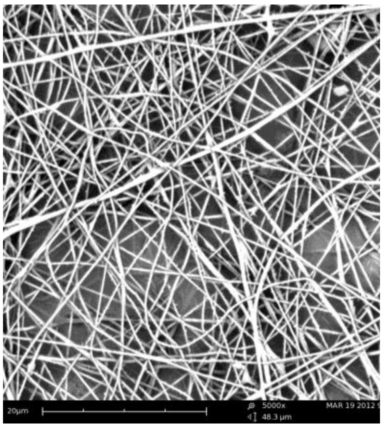
5%PEO+1,5%NaCl (SEM 5000x)



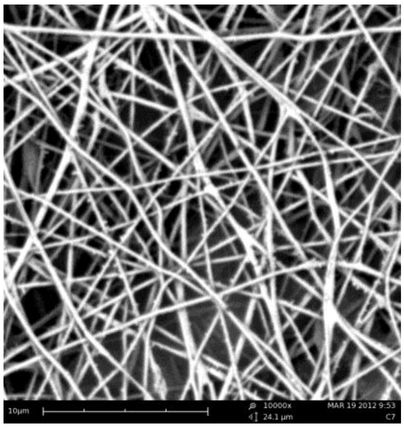
5%PEO+1,5%NaCl (SEM 10000x)



5%PEO+2%NaCl (SEM 1000x)



5%PEO+2%NaCl (SEM 5000x)



5%PEO+2%NaCl (SEM 10000x)